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Kerfoot

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(54) **COATED MICROBUBBLES FOR TREATING AN AQUIFER OR SOIL FORMATIONS**

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(51) **Int. Cl.**
C02F 1/78 (2006.01)

(52) **U.S. Cl.** **252/186.21**; 210/759; 210/760; 210/763; 252/186.28; 423/581; 423/582

(58) **Field of Classification Search** 252/186.28
See application file for complete search history.

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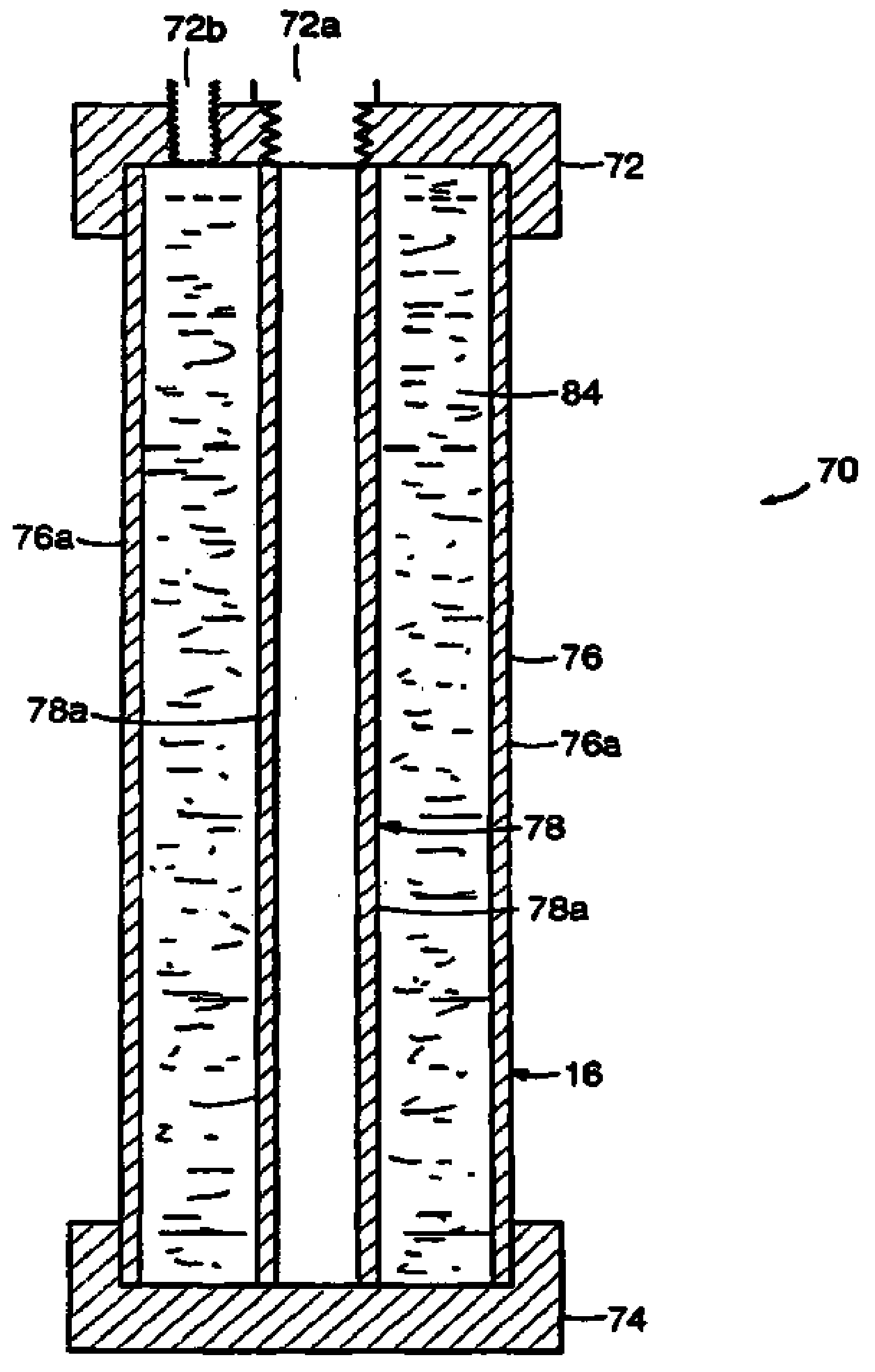
(57) **ABSTRACT**

A microporous diffuser includes a first elongated member including at least one sidewall having a plurality of microscopic openings. The sidewall defines an interior hollow portion of the member. The diffuser has a second elongated member having a second sidewall having a plurality of microscopic openings, the second member being disposed through the hollow region of the first member. The diffuser includes an end cap to seal a first end of the microporous diffuser and an inlet cap disposed at a second end of microporous diffuser for receiving inlet fittings.

21 Claims, 12 Drawing Sheets



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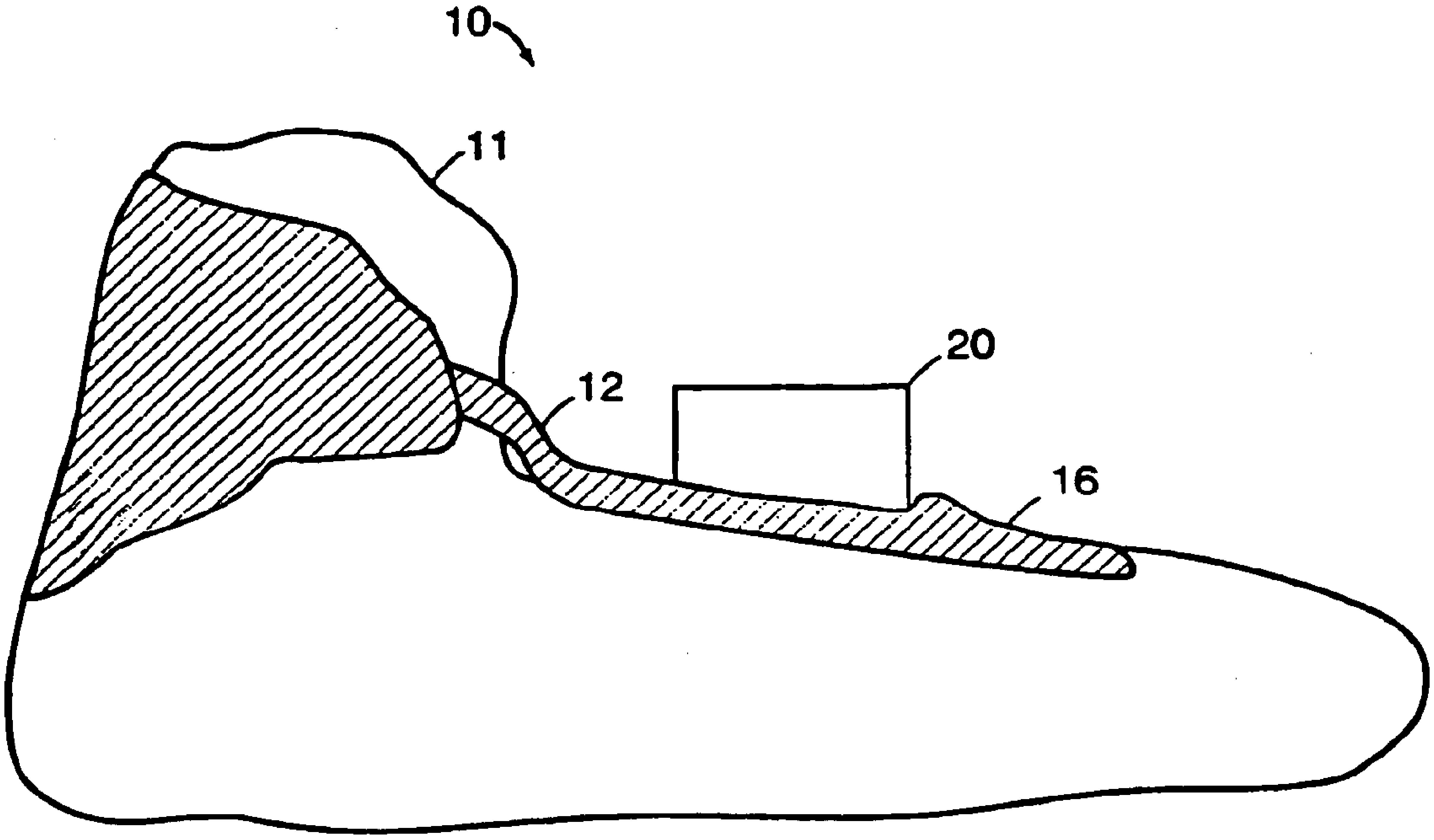
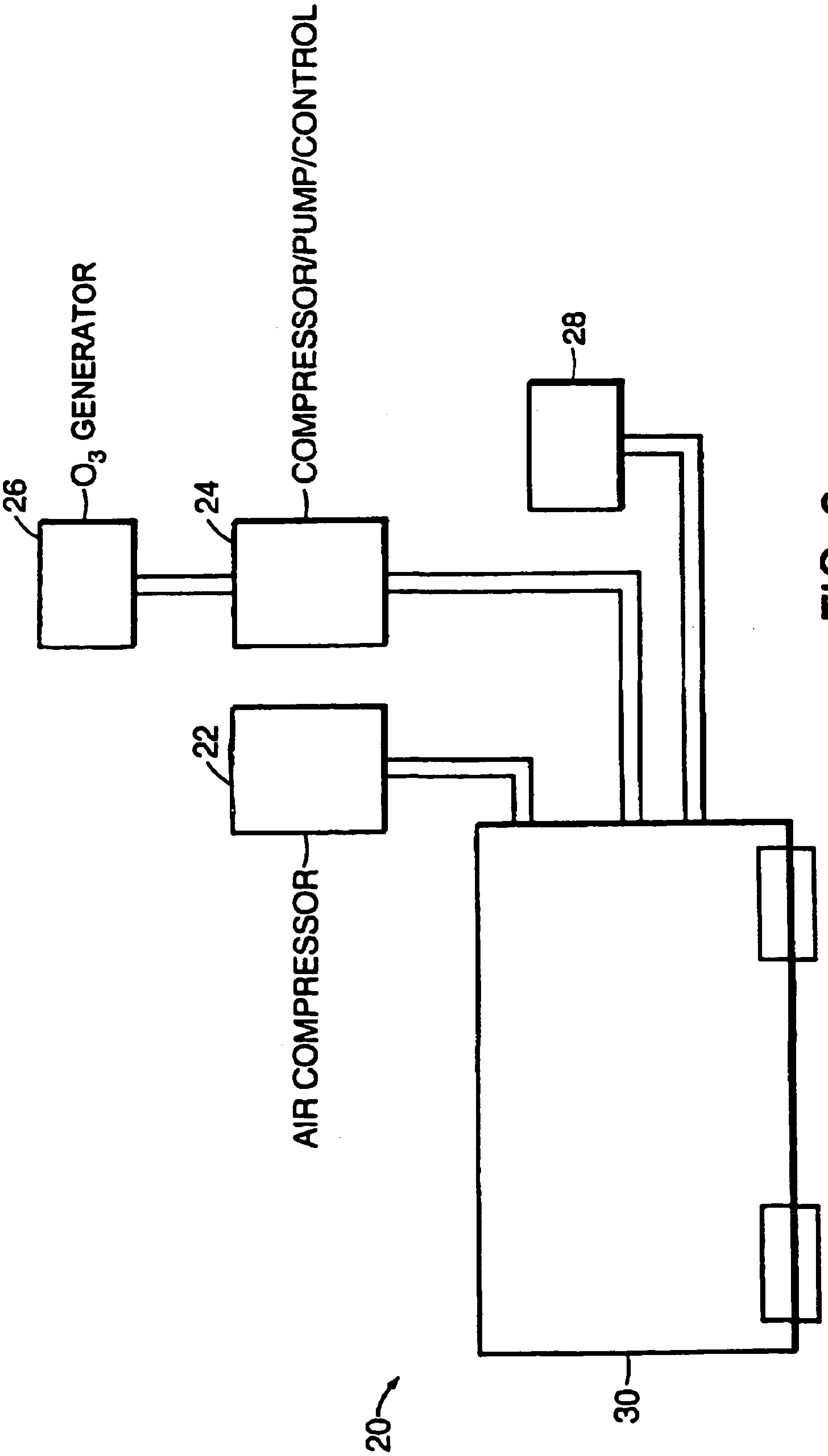


FIG. 1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O_3 GENERATOR
24
COMPRESSOR/PUMP/CONTROL
28
22
AIR COMPRESSOR
30
20

FIG. 2

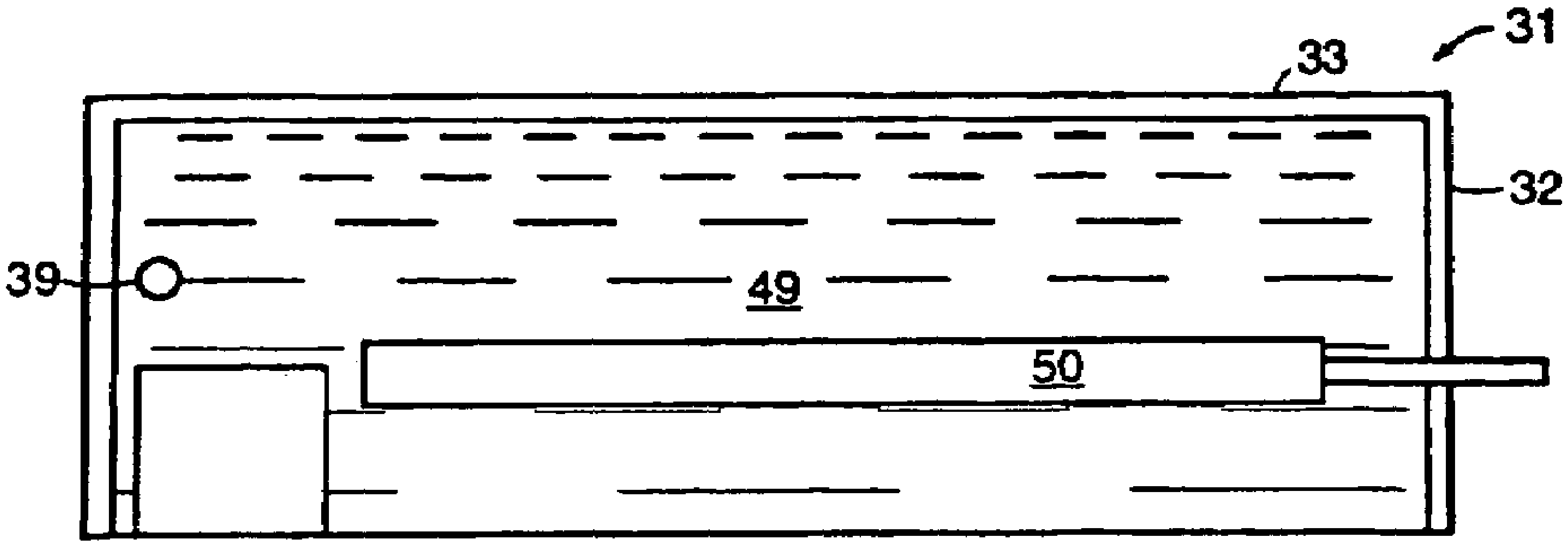

31
33
32
39
49
50

FIG. 3B

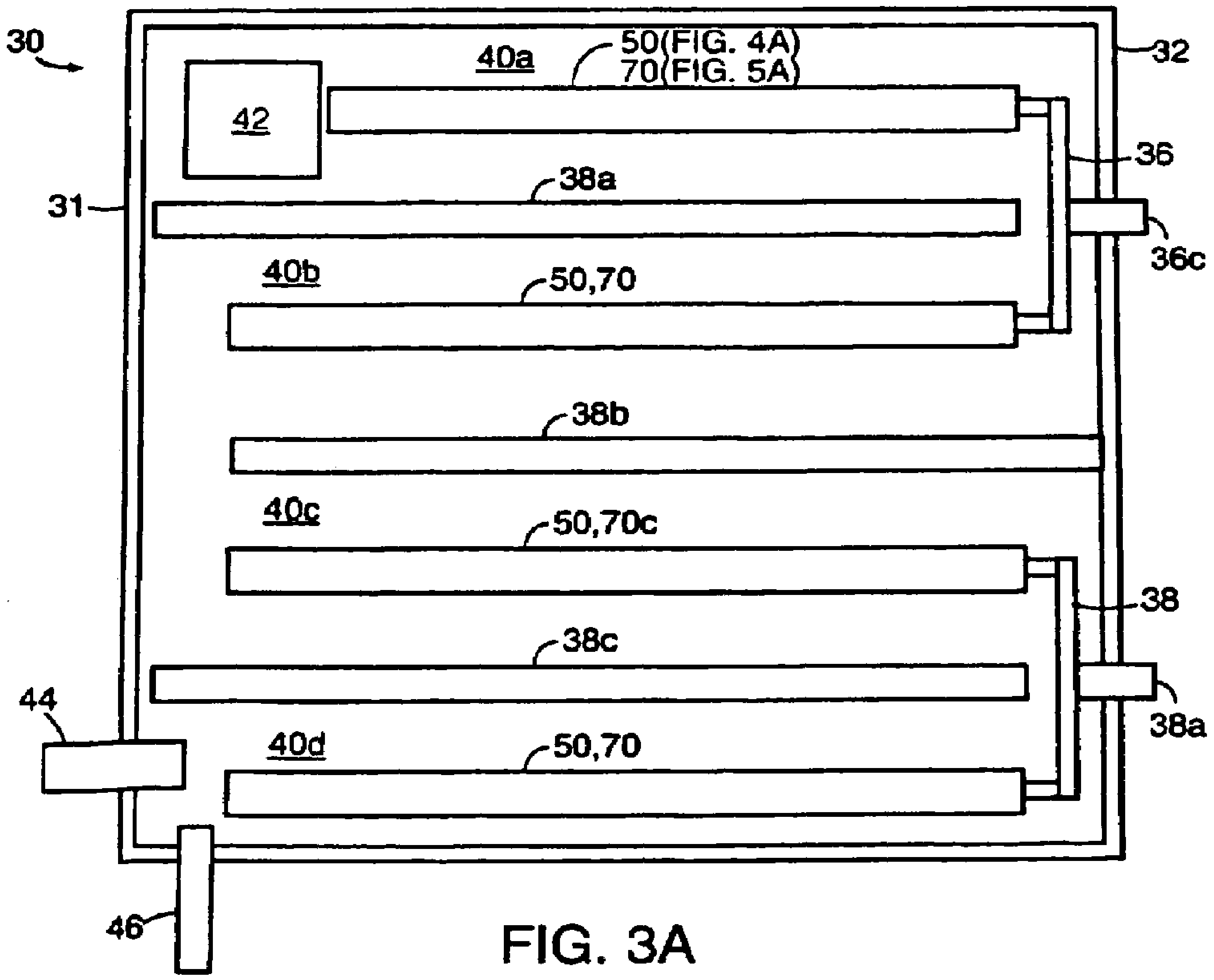

30
32
40a
50(FIG. 4A)
70(FIG. 5A)
42
36
31
38a
36c
40b
50,70
38b
40c
50,70c
38
38c
38a
44
40d
50,70
46

FIG. 3A

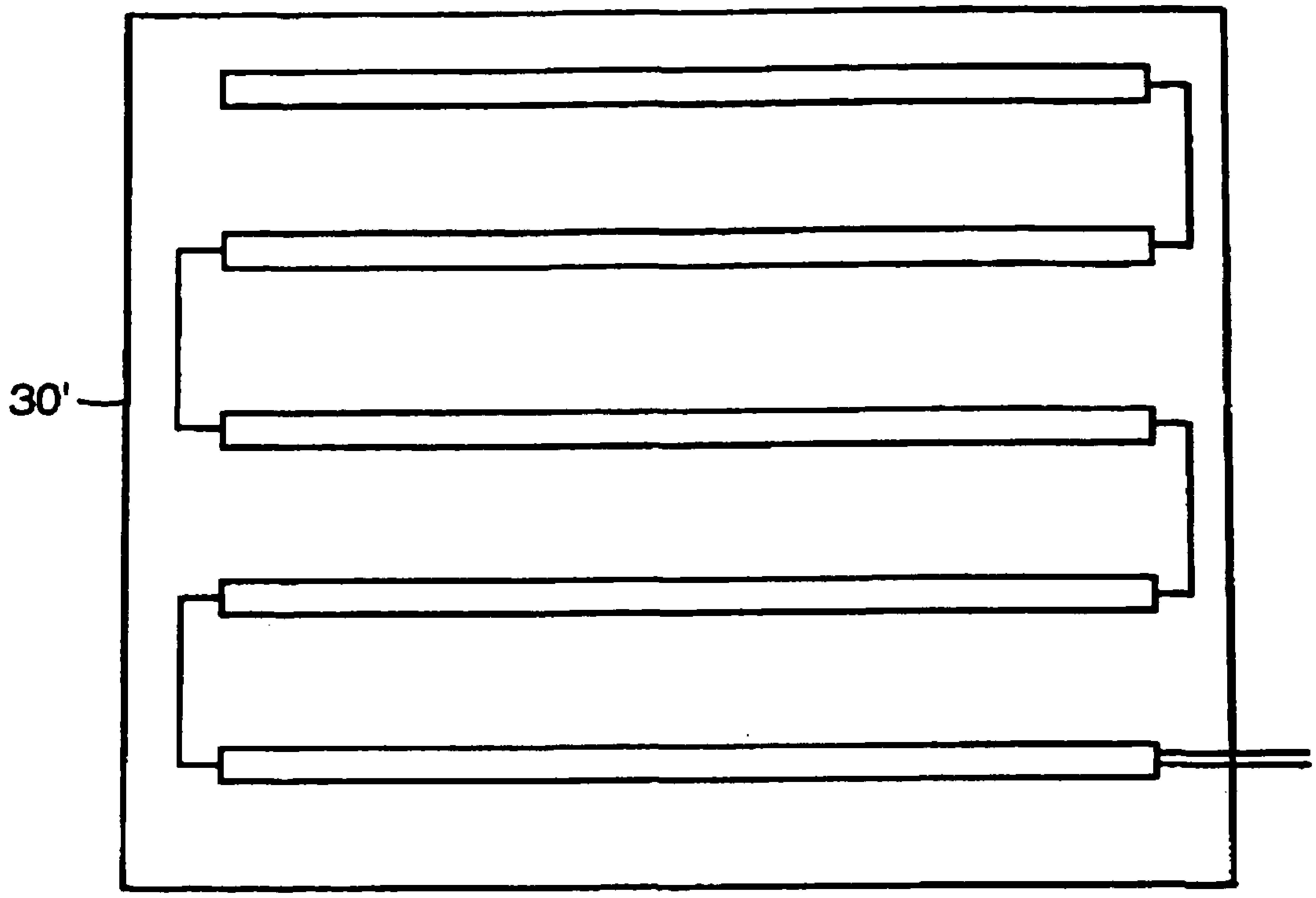


FIG. 3C

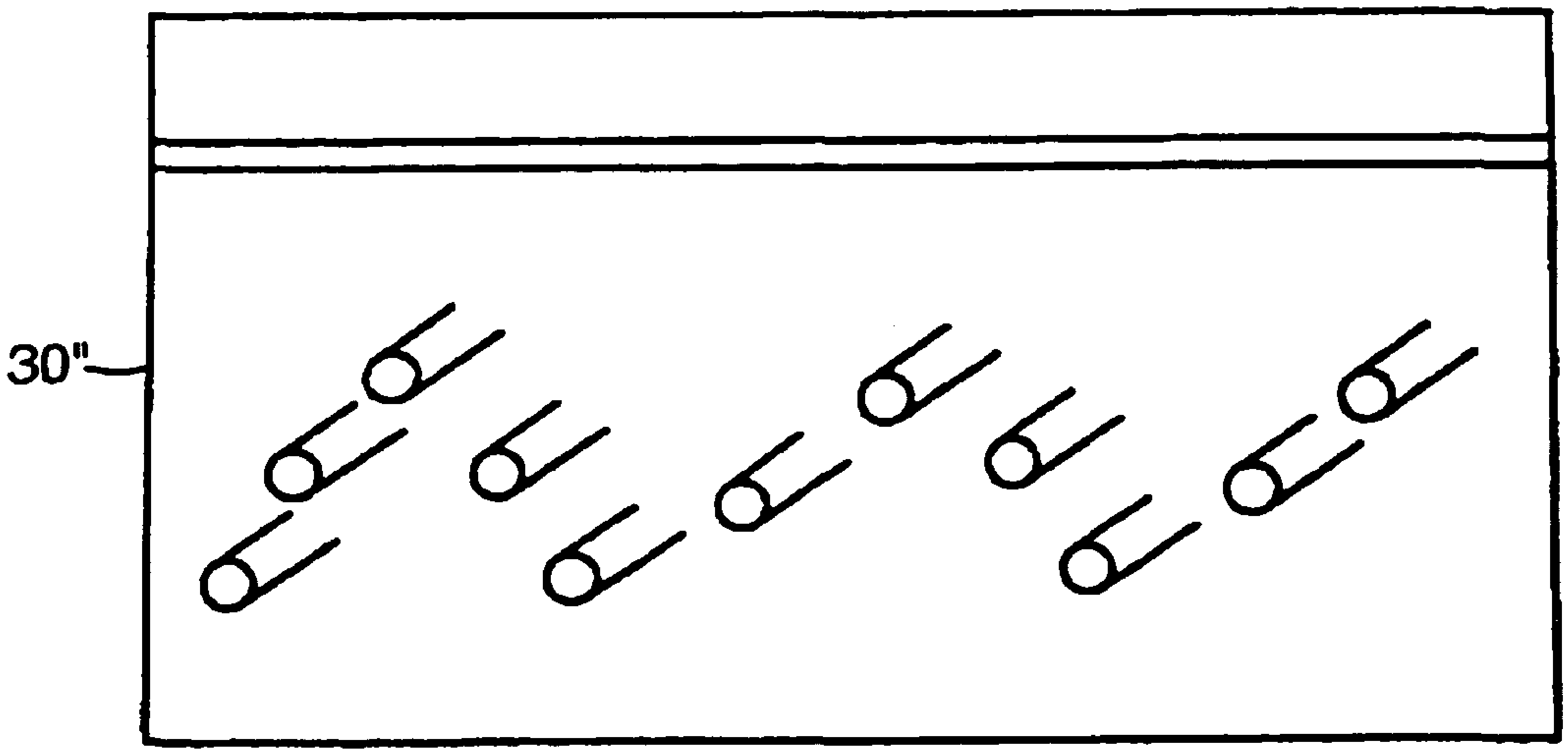


FIG. 3D

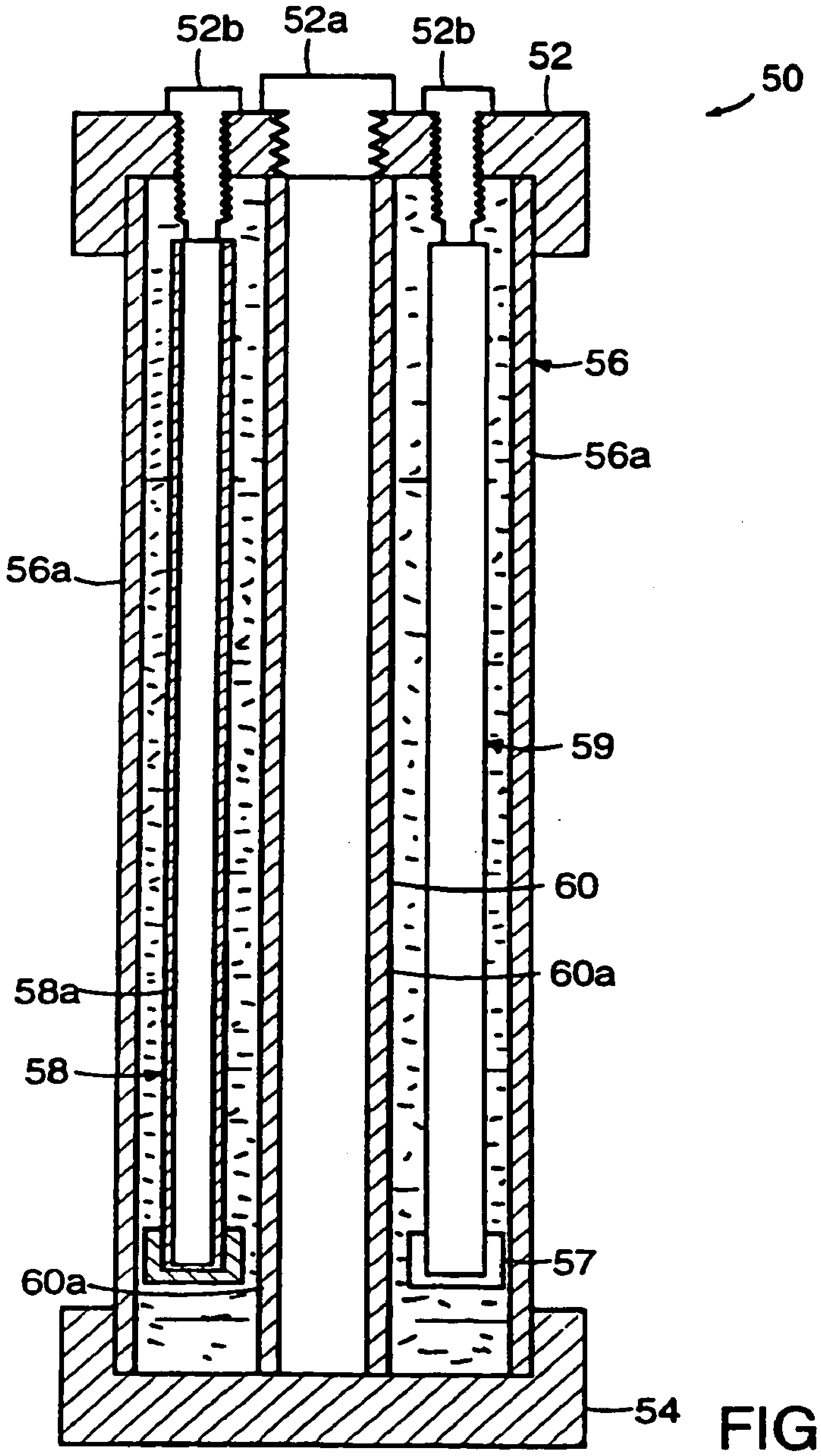


FIG. 4A

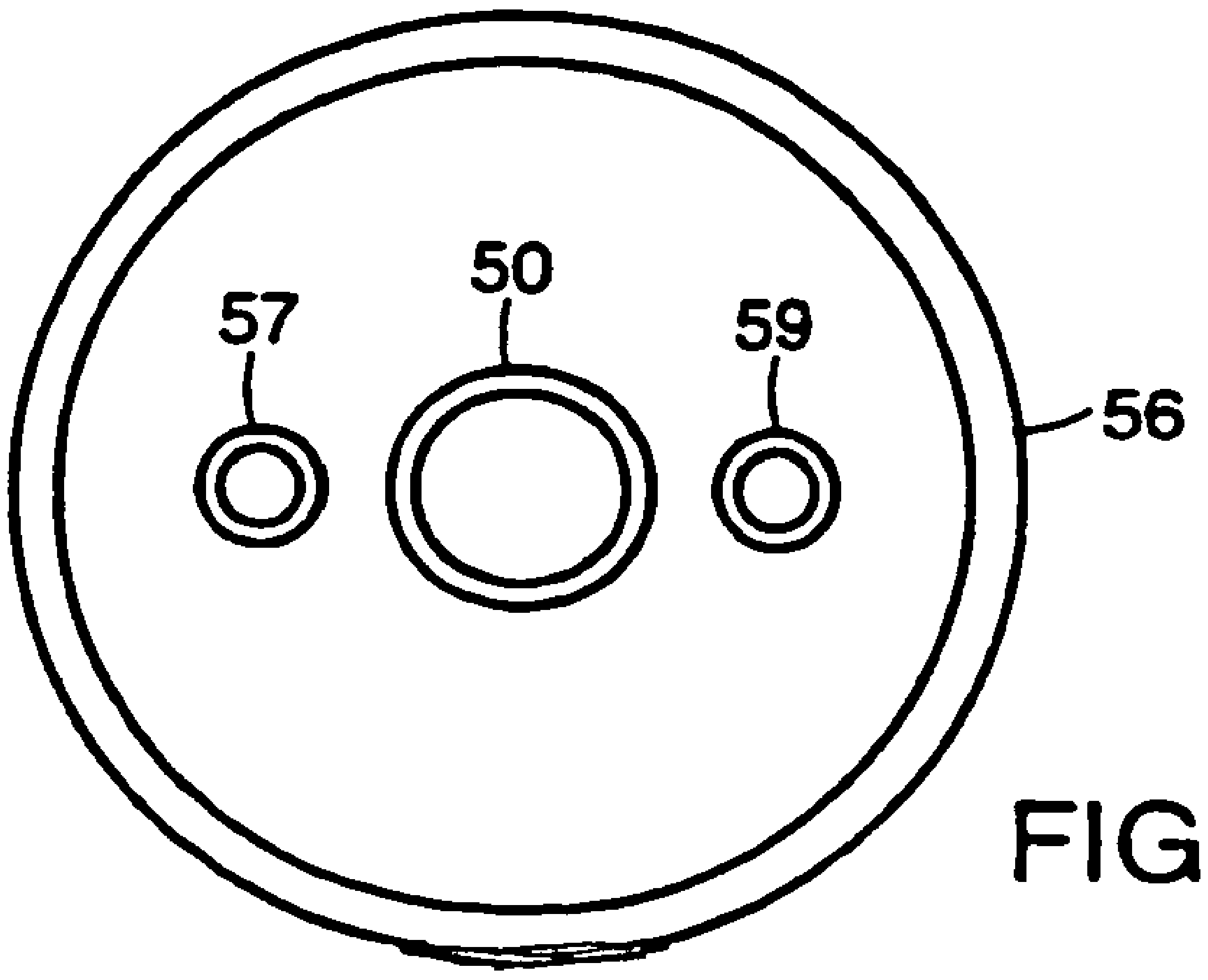


FIG. 4B

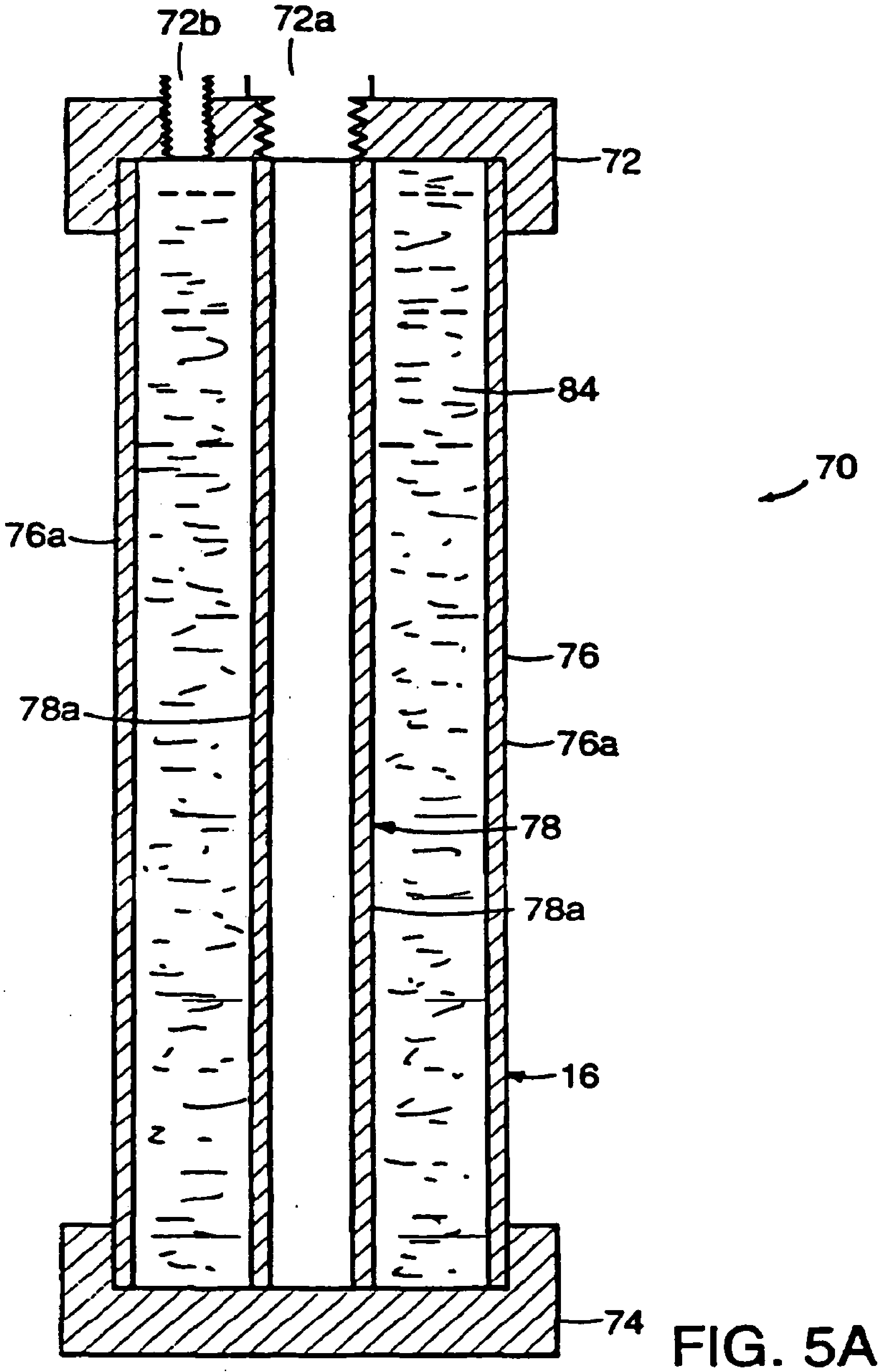


FIG. 5A

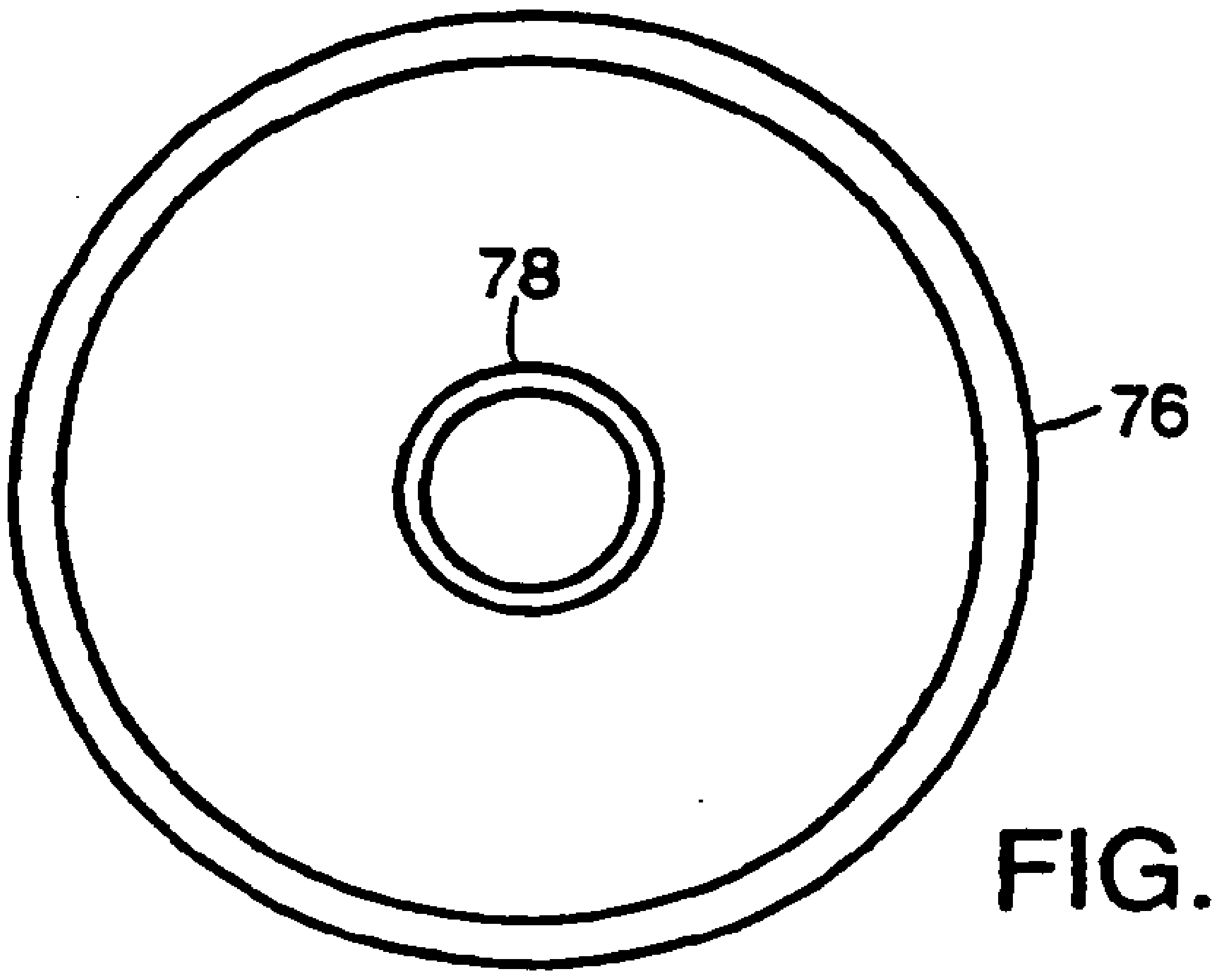


FIG. 5B

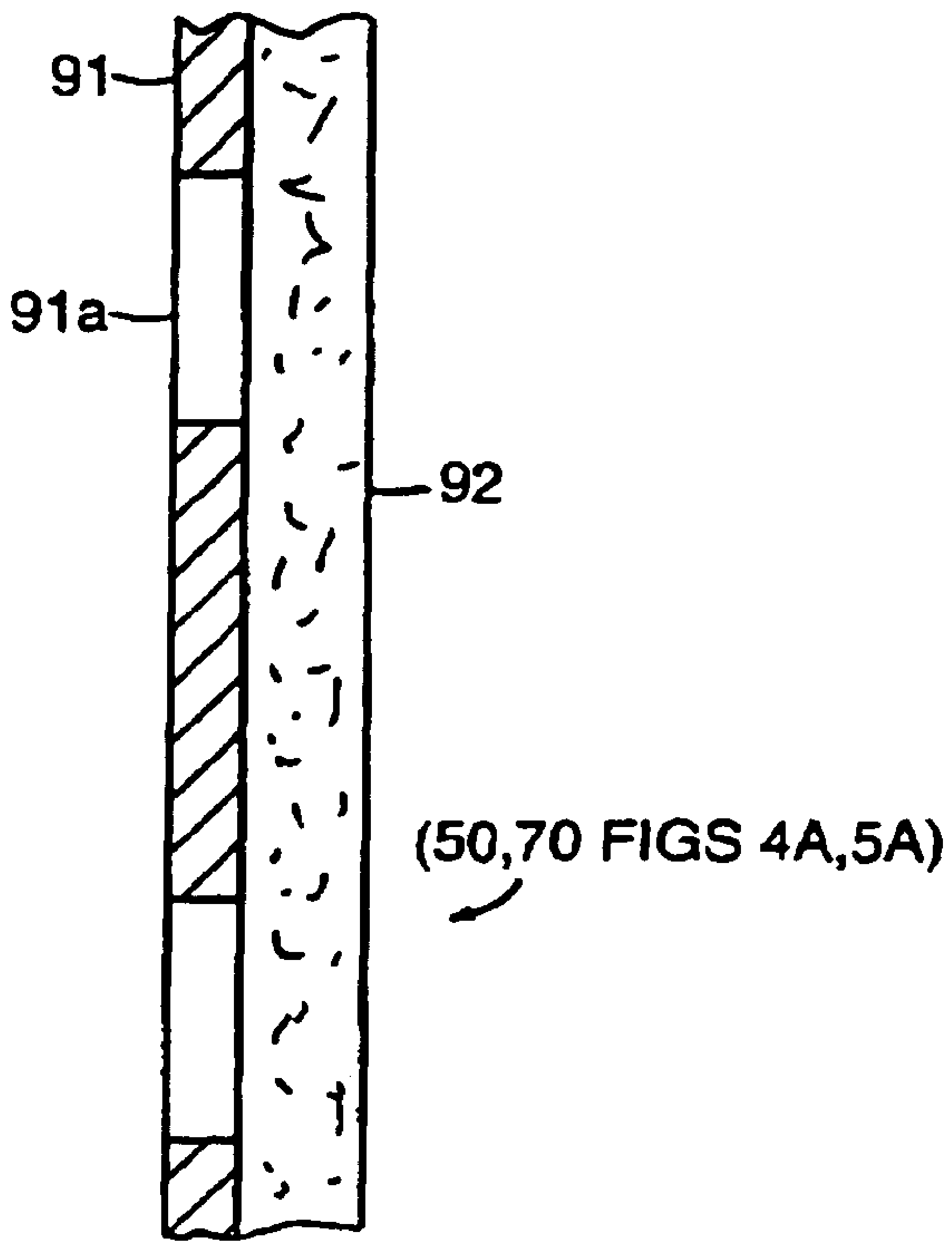


FIG. 6A

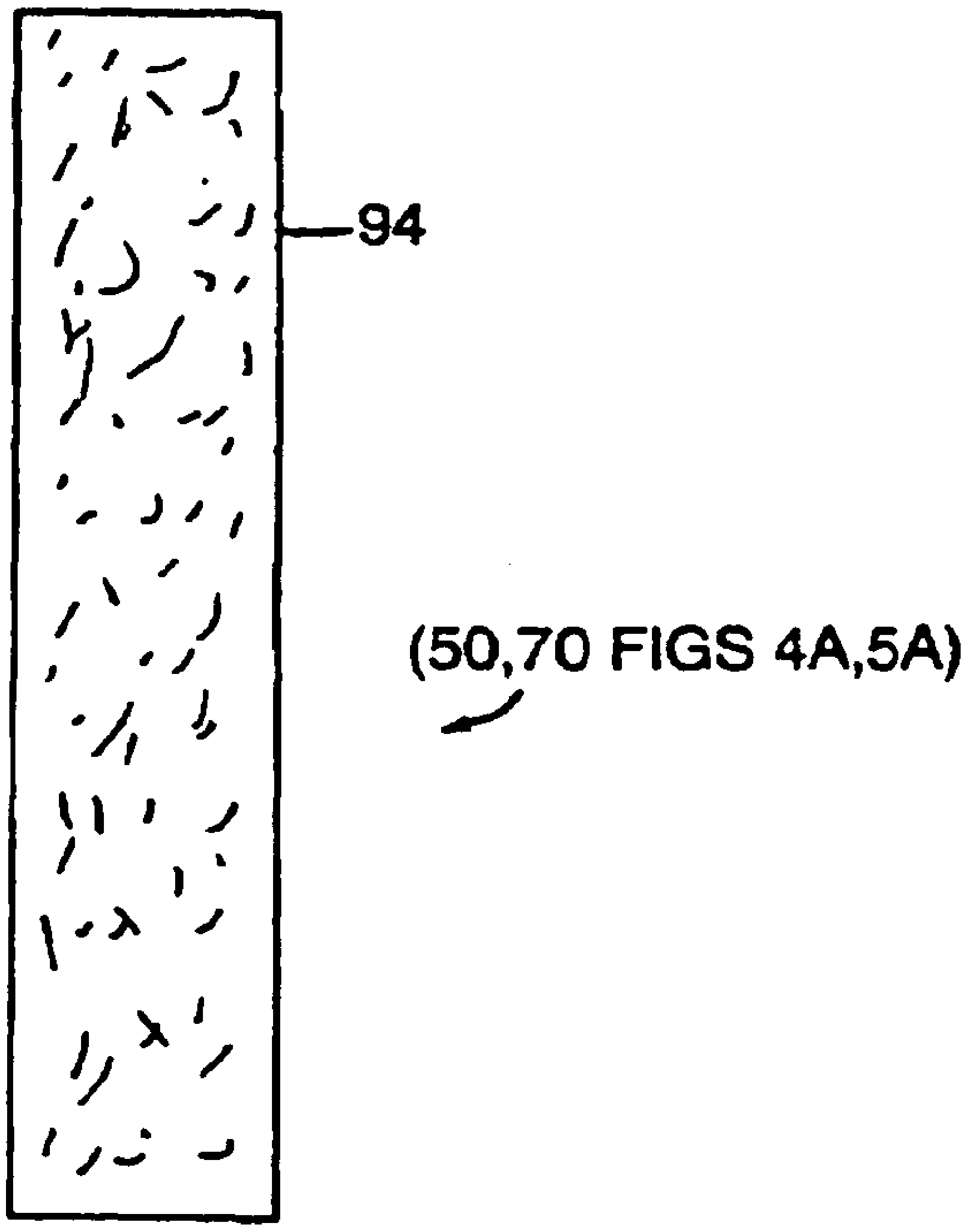


FIG. 6B

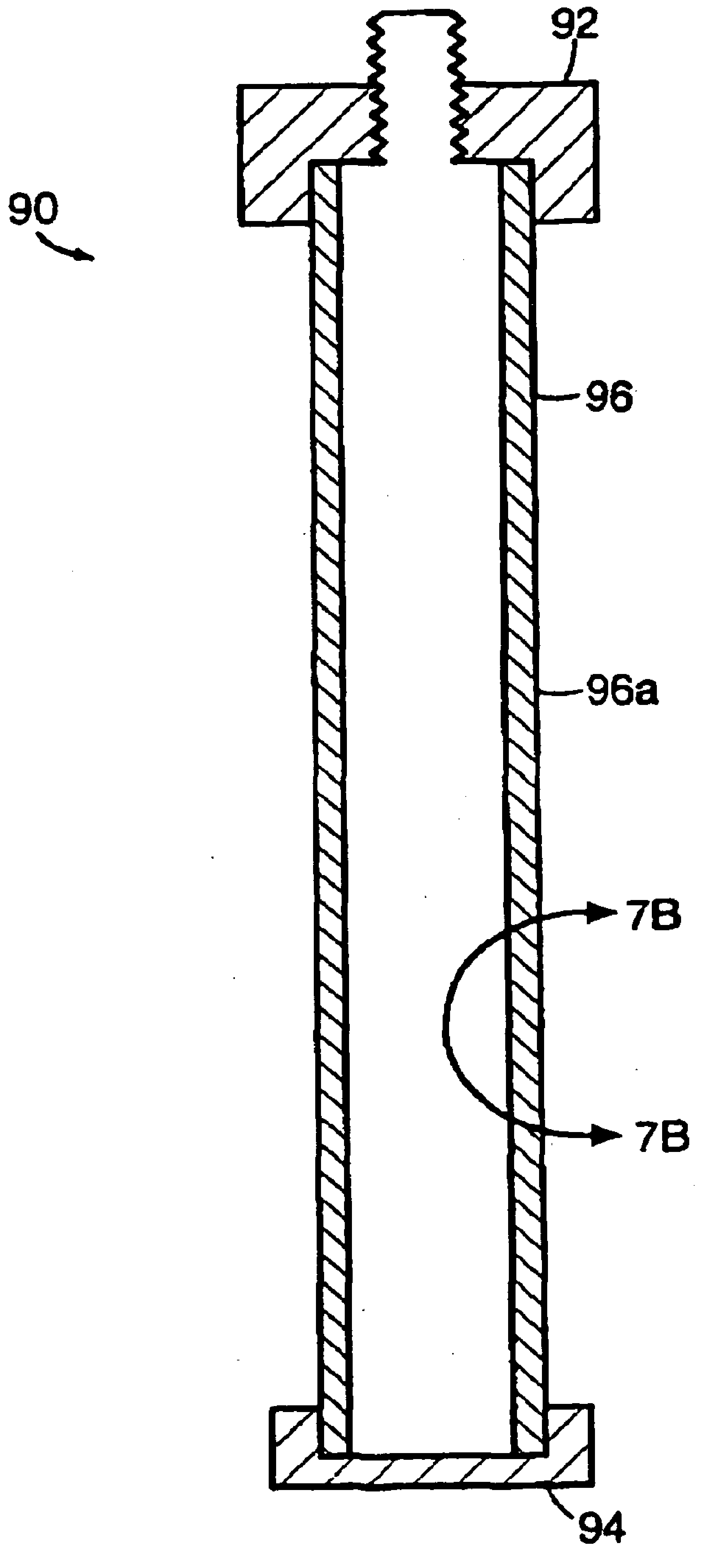


FIG. 7A

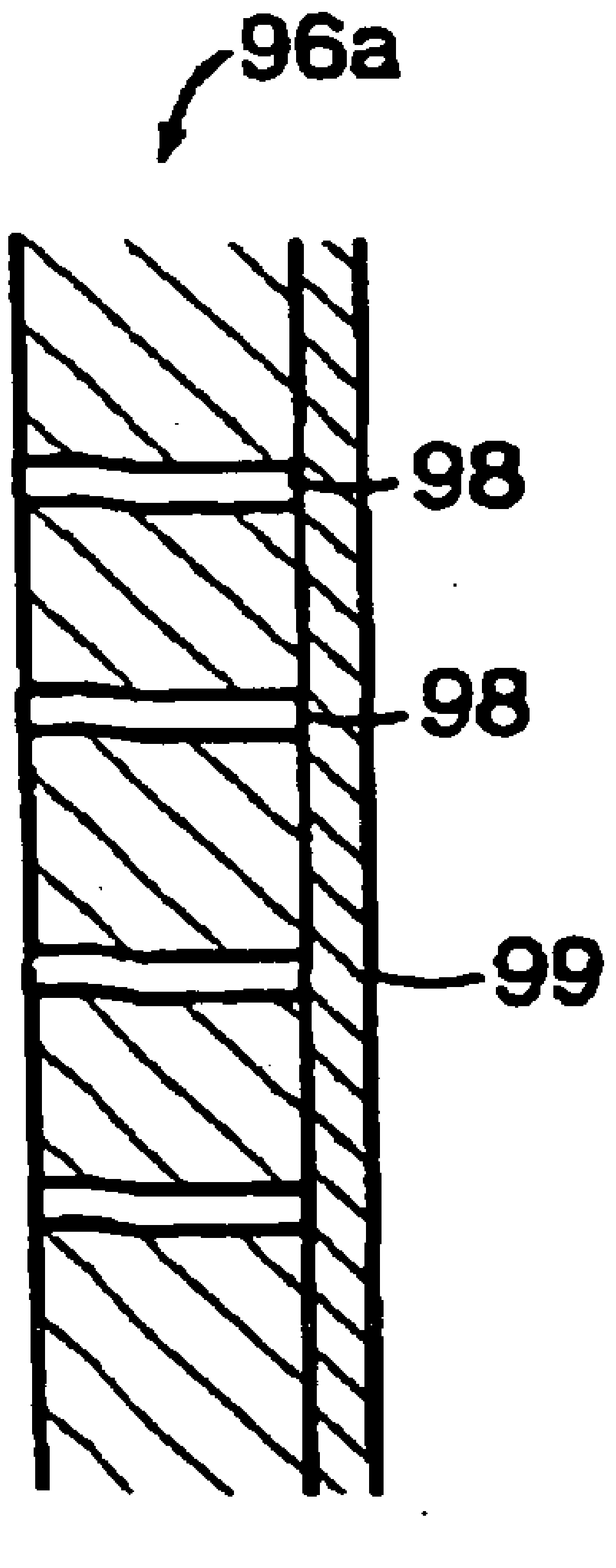


FIG. 7B

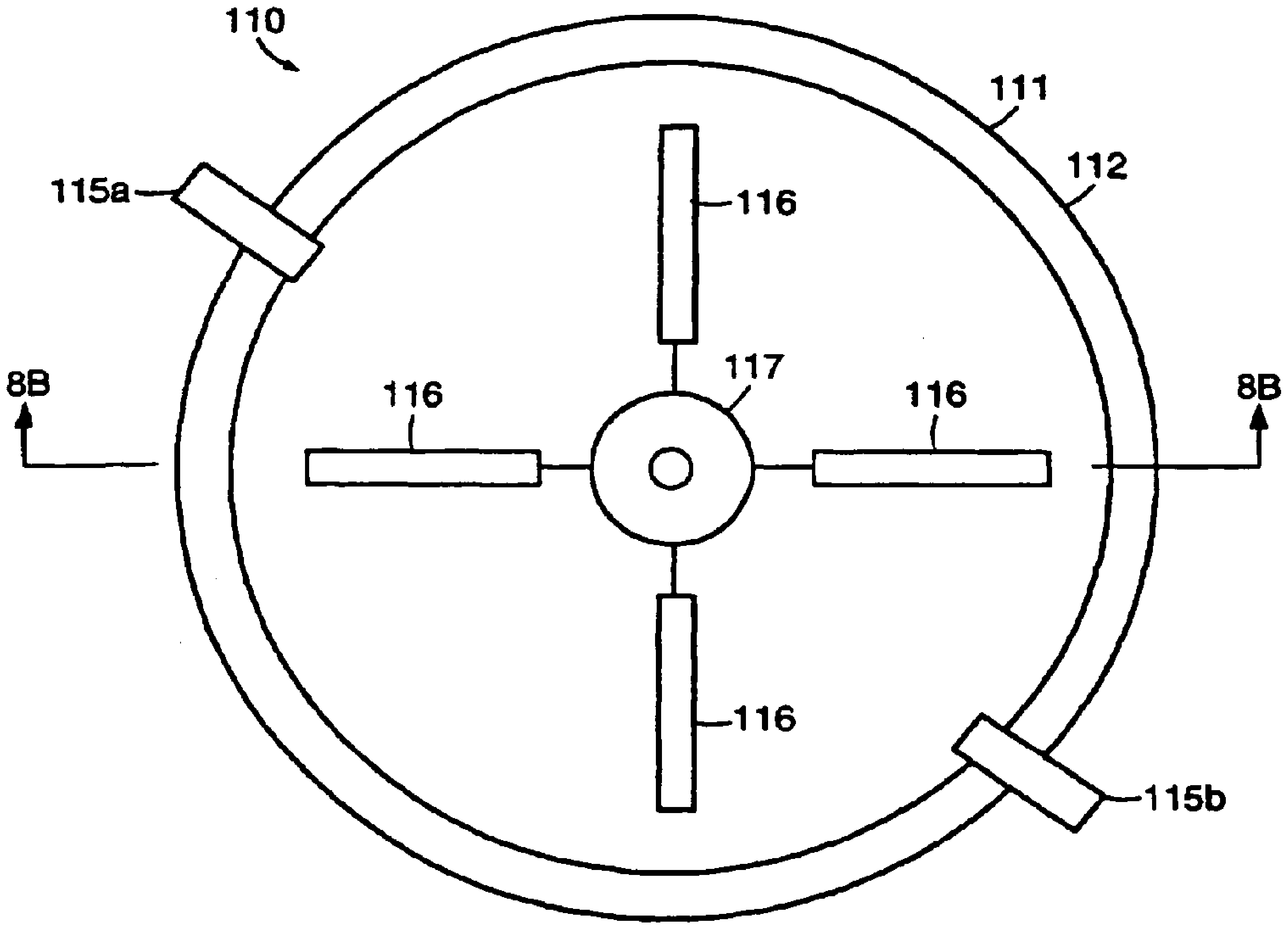


FIG. 8A

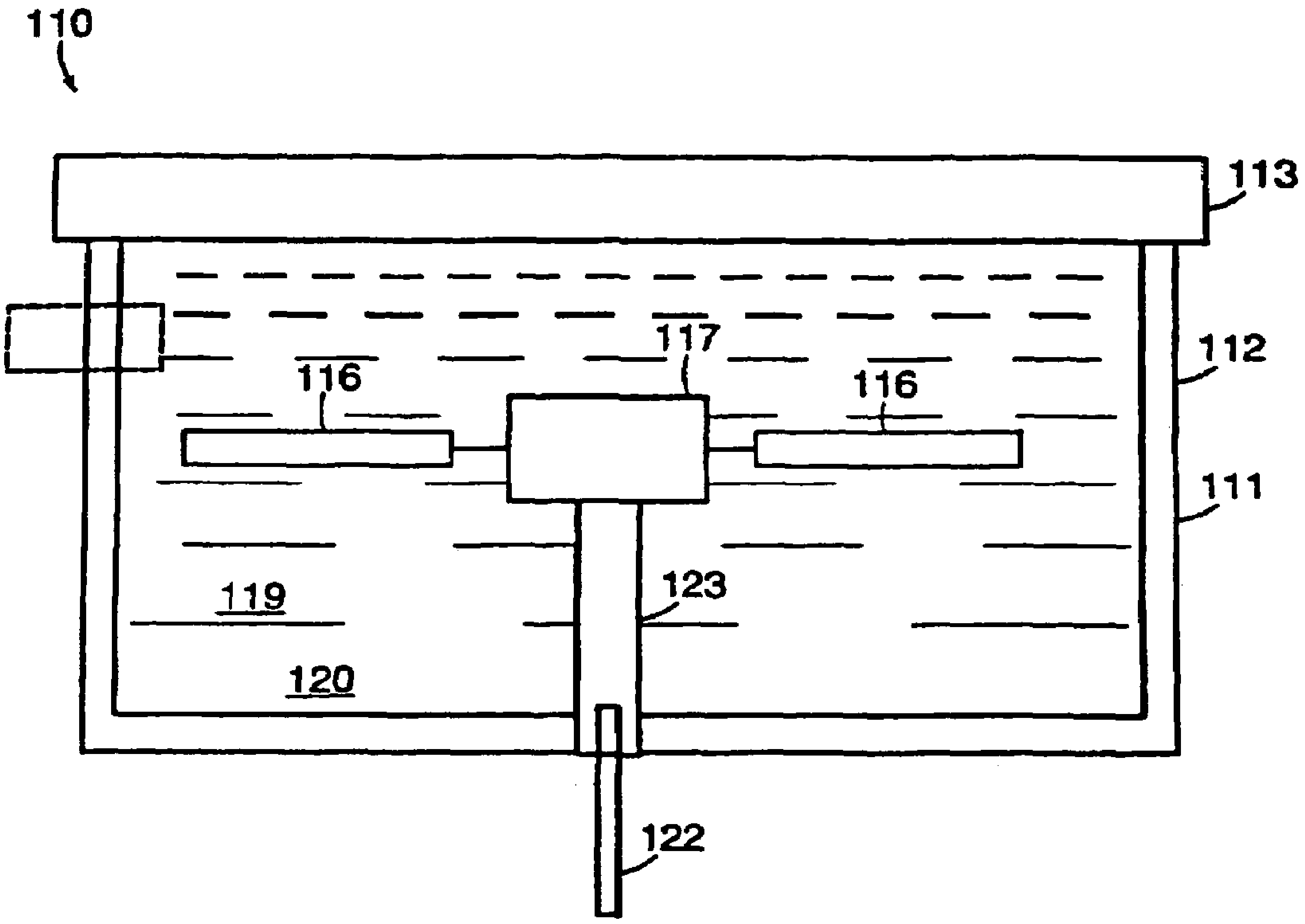


FIG. 8B

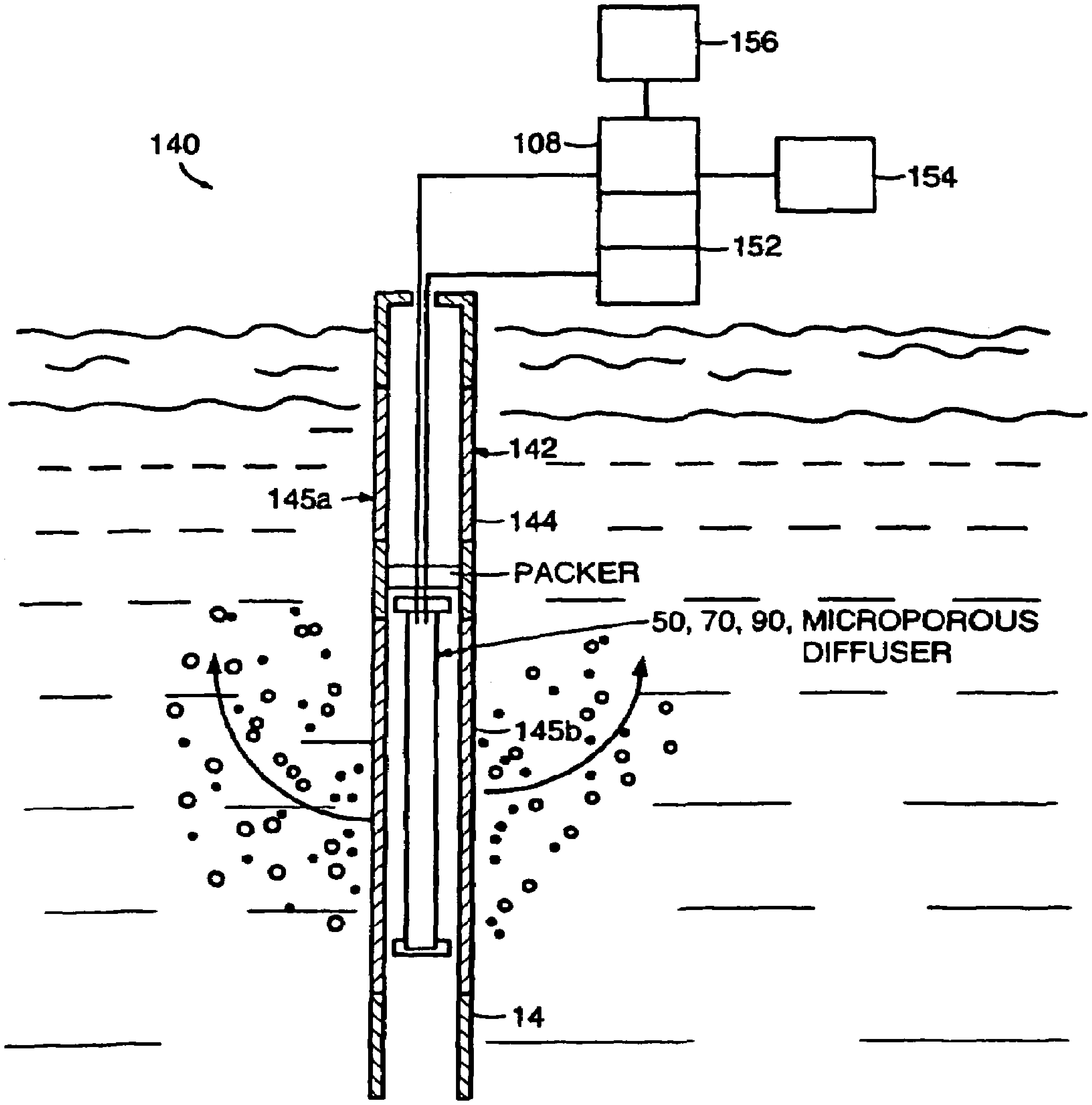

156
140
108
154
152
142
145a
144
PACKER
50, 70, 90, MICROPOROUS DIFFUSER
145b
14

FIG. 9

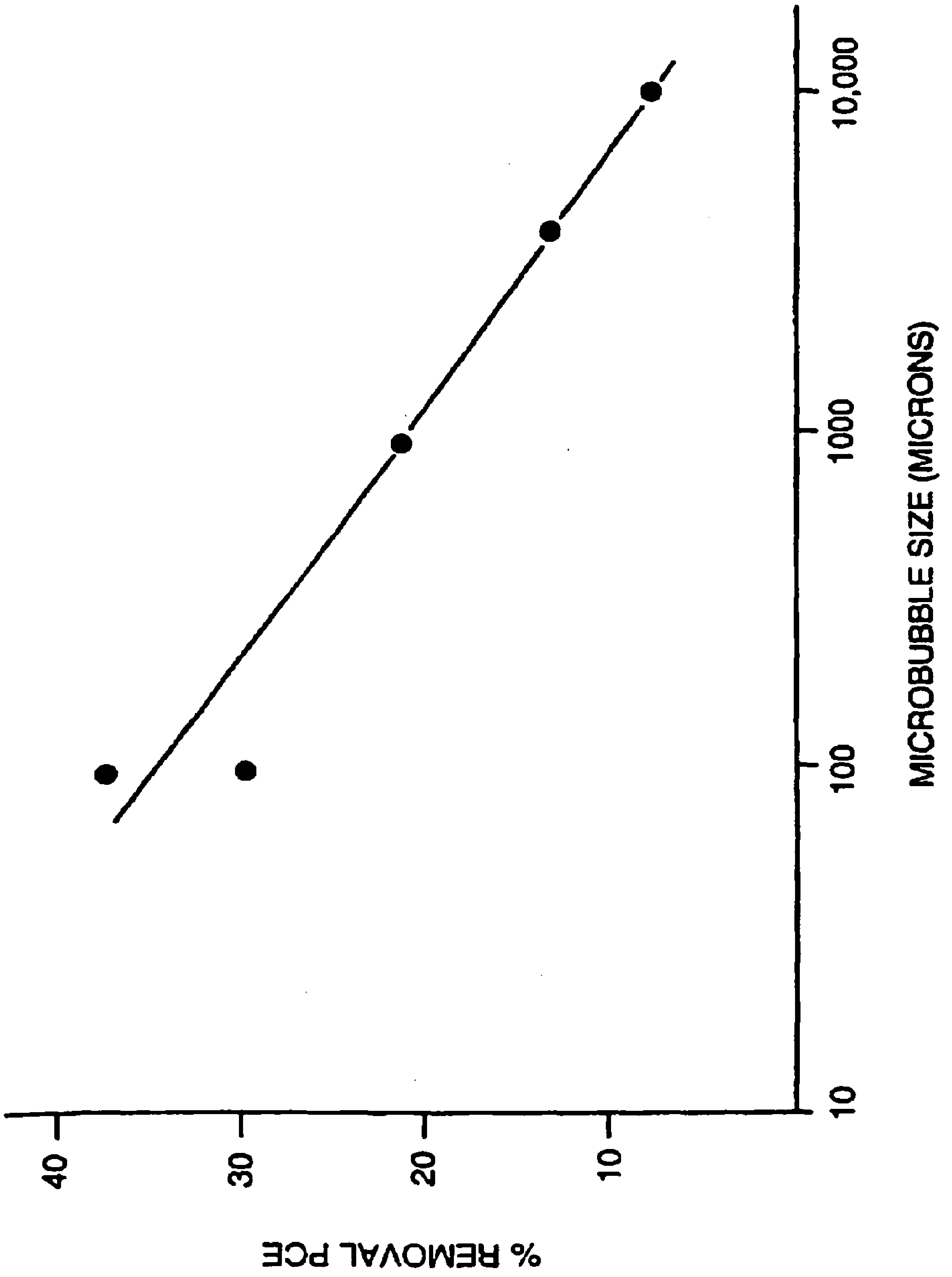

% REMOVAL PCE
40
30
20
10
10
100
1000
10,000
MICROBUBBLE SIZE (MICRONS)

FIG. 10

COATED MICROBUBBLES FOR TREATING AN AQUIFER OR SOIL FORMATIONS

This application is a divisional application of application Ser. No. 10/910,441 filed on Aug. 2, 2004 now U.S. Pat. No. 6,984,329, which was a continuation of application Ser. No. 10/354,584 filed Jan. 30, 2003 (now U.S. Pat. No. 6,780, 329), which was a divisional of application Ser. No. 10/223, 166 filed on Aug. 19, 2002 (U.S. Pat. No. 6,596,161), which was a continuation of application Ser. No. 09/470,167, filed Dec. 22, 1999 (U.S. Pat. No. 6,436,285).

BACKGROUND

This invention relates generally to water remediation systems.

There is a well recognized need to clean-up contaminants that exist in ground and surface water. In particular, there is one type of contamination problem which widely exists, that is, the contamination of surface waters or subsurface waters which find their way to the surface such as, for example, in a contaminated spring. Such surface waters may be contaminated with various constituents including volatile hydrocarbons, such as chlorinated hydrocarbons including trichloroethene (TCE), tetrachloroethene (PCE).

SUMMARY

According to an additional aspect of the present invention, a microporous diffuser includes a first elongated member including at least one sidewall having a plurality of microscopic openings, said sidewall defining an interior hollow portion of said member and a second elongated member having a second sidewall having a plurality of microscopic openings, said second member being disposed through the hollow region of said first member. The diffuser includes an end cap to seal a first end of the microporous diffuser and an inlet cap disposed at a second end of microporous diffuser for receiving inlet fittings.

According to an additional aspect of the present invention, a microporous diffuser includes a first hollow cylindrical tube having a sidewall comprising a plurality of microscopic openings and a second hollow tube having a sidewall having a plurality of microscopic openings, said second tube being disposed through said first tube. The diffuser also includes an end cap to seal ends of said tubes and an inlet cap disposed to provide inlets to interior portions formed by sidewalls of said tubes.

According to a still further aspect of the invention, a microporous diffuser includes a first hollow cylindrical tube coupled to a first inlet and adapted to be fed by a gas, the tube having a sidewall comprising a plurality of microscopic openings the openings having a diameter in a range of 1 to 200 microns and a second hollow tube coupled to a second inlet and adapted to be fed by a liquid, the tube having a sidewall with a plurality of microscopic openings, the openings having a diameter in a range of 1 to 200 microns, with the first tube being disposed through the second tube and arranged such that gas injected into the first tube travels towards the sidewall of the second tube forming microfine bubbles laminated with the liquid. The diffuser also includes an end cap to seal first ends of the tubes and an inlet cap disposed to seal second ends of said tubes and to support the first and second inlets to the interior portions formed between the tubes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a diagrammatical view of a typical surface water treatment example.

FIG. **2** is a block diagram of an apparatus used in the treatment process.

FIGS. **3**A and **3**B are respectively plan and elevational views somewhat schematic, of a spring box used in the apparatus of FIG. **2**.

FIGS. **3**C and **3**D are plan and elevational views of still alternate spring box arrangements.

FIGS. **4**A and **4**B are longitudinal cross-section and plan cross-sectional views of a microporous diffuser useful in the spring box of FIGS. **3**A and **3**B;

FIGS. **5**A, **5**B are longitudinal cross-section and plan cross-sectional views, respectively, of an alternative microporous diffuser useful in the spring box of FIGS. **3**A and **3**B.

FIGS. **6**A and **6**B are cross-sectional view of sidewalls of the microporous diffusers of either FIGS. **4**A, **4**B or **5**A, **5**B showing exemplary construction details.

FIGS. **7**A, **7**B are longitudinal cross-section and plan cross-sectional views, respectively, of a still alternative microporous diffuser useful in the spring box of FIGS. **3**A-**3**D.

FIGS. **8**A and **8**B are respectively plan and elevational views somewhat schematic, of a circular spring box arrangement with a mixing feature also useful in the apparatus of FIG. **2**.

FIG. **9** is a cross-sectional view showing an alternative treatment example.

FIG. **10** is a plot of removal rate of PCE for an aqueous solution equivalent to 120 ppb, over differing bubble sizes.

DETAILED DESCRIPTION

Referring now to FIG. **1**, an example 10 of the use of an apparatus for treatment of surface water or in-situ removal of contaminants from water is shown. Illustrated in FIG. **1** is a site **11**, having a subsurface aquifer **14** that produces surface waters **12** such as by a spring. A spring-box treatment system **20** disposed on the site **11**. The spring box treatment system **20** is disposed to intercept the surface water **12** and to divert the surface water into the spring box treatment system **20** to remove contaminants such as volatile hydrocarbons and, in particular, chlorinated hydrocarbons which may exist in the water in the aquifer **14**. The spring box treatment system **20** outputs a water stream **16** which is substantially free of the contaminants.

Contaminants which can be treated or removed by use of the spring box treatment system **20** include hydrocarbons and, in particular, volatile chlorinated hydrocarbons such as tetrachloroethene, trichloroethene, cisdichloroethene, trans-dichloroethene, 1-1-dichloroethene and vinyl chloride. In particular, other materials can also be removed from the stream including chloroalkanes, including 1,1,1 trichloroethane, 1,1, dichloroethane, methylene chloride, and chloroform; benzene, toluene, ethylbenzene, O-xylene, P-xylene, naphthalene and methyltetrabutylether (MTBE). It should be understood that the use of the spring-box treatment system **20** is not limited to flowing surface water but could be used to treat pumped or stored water.

Referring now to FIG. **2**, the spring box treatment system **20** includes a spring box **30**, and an air compressor **22**, a compressor/pump control mechanism **24**, and an ozone (O_3) generator **26**. The air compressor **24** can feed a stream of air into the spring box **30** whereas, the compressor pump control **24** feeds a stream of air mixed with ozone (O_3) from the ozone generator **26** into the spring box **30** to affect substantial removal of the above-mentioned or similar types of contaminants. Optionally, or in addition thereto, the apparatus **20** can also include a pump **28** that supplies a liquid decontamination agent such as hydrogen peroxide or catalyst agents including iron containing compounds such as iron silicates or palladium or palladized carbon. To promote biodegradation reactions, the liquid introduced can be a nutrient mixture of nitrogen (ammonium or nitrate), phosphorus, and potassium along with oxygen as a gas to promote oxic reactions or carbon dioxide and hydrogen sulfide to promote reduction reactions.

The spring box **30** uses primarily a gas-gas reaction between contaminant vapors and ozone (described below). This reaction can be supplemented with a liquid phase reaction. A liquid decontaminator such as hydrogen peroxide can also be used. The use of hydrogen peroxide as a thin film coating on the bubbles promotes the decomposition rate by adding a secondary liquid phase reactive interface as volatile compounds enter the gaseous phase. It also expands the types of compounds that can be effectively removed. Alternatively, the pump control **28** can simply feed water.

Referring now to FIGS. **3**A and **3**B, an arrangement of a spring box **30** is shown. The spring box includes a container **31** comprised of a sidewall **32** of a durable material such as concrete over which is disposed or attached a water tight lid **33** also comprised of concrete. Within the spring box **30** is provided an inlet port **42** to receive the water from the spring, as well as a plurality of partially closed chambers **40***a*-**40***d* which are formed within the interior of the spring box by walls or partitions **38***a*-**38***c*. Within each of the chambers **40***a*-**40***d* are disposed a plurality of microporous diffusers such as those shown in conjunction with my issued U.S. Pat. No. 5,855,775 which is incorporated herein by reference. Alternatively, microporous diffusers **50**, **70**, as described below in conjunction with FIGS. **4**A and **4**B or FIGS. **5**A and **5**B may be used.

In the arrangement shown in FIG. **3**A, a first pair of microporous diffusers **50***a*, **50***b* or **70***a*, **70***b* are coupled to a common gas/liquid feed arrangement **36***a* which can be fed, for example, from compressor/pump **24** and compressor **28** (FIG. **2**). The spring box **30** also includes a second feed arrangement **38***b* which in this embodiment has one of the microporous diffusers **50***c*, **70***c* being fed with a combination of air, ozone and air, ozone and liquid as above, and with the second microporous diffuser **50***d*, **70***d* being fed only by air to provide air stripping of any residual ozone before exiting of the treated water.

As shown in FIG. **3**B, the microporous diffusers are arranged in elevation above the bottom of the spring box **30** within a pool **39** of water provided from the spring or other surface water source.

FIGS. **3**C and **3**D show still alternate spring box arrangements. In the arrangement **30'** of FIG. **3**C, the diffusers **50** or **70** are coupled in series whereas FIG. **3**D shows diffusers **50**, **70** arranged to be staggered in elevation over the height of the spring box.

The spring box **30** is an ozone reactor vessel in which ozone is pumped into the pool of water through the use of the microporous diffusers. The microporous diffusers are disposed in the water under treatment and transfer ozone into the water in the form of microfine or fine bubbles which promote rapid gas/gas/water reactions with volatile organic compounds particularly in the presence of a catalyst or enhancer which may participate in the gaseous phase of the reaction, instead of solely enhancing dissolved aqueous disassociation and reactions. In addition, with the optional use of the liquid port to the apparatus, the gas/gas reactions are optimized to include gas/gas reactions within the gaseous phase as well as inducing water aqueous phased reactions to achieve an overall decomposition rate within the gaseous phase and the aqueous phase from second water reactions. For example, the use of hydrogen peroxide as a laminate coating on the bubbles can enhance decomposition rates as mentioned below. The micron plastic bubblers may also be coated with or have sintered into construction an outer layer of activated carbon or activated carbon with palladium to simultaneously accumulate and promote decomposition of the chloroethenes.

The production of microbubbles and selection of appropriate size distribution are selected for optimized gas exchange through high surface area to volume ratio and long residence time within the liquid to be treated. The microbubbles are generated by using microporous materials in the microporous diffuser **50** that acts as a bubble chamber, as shown in the embodiment **50** (FIG. **4**A-**4**B) or, alternatively, through the embodiment **70** of the microporous diffuser of FIG. **5**A-**5**B. The apparatus **20** promotes the continuous production of microbubbles minimizing coalescing or adhesion. The injected air/liquid combination moves as a fluid into the water to be treated; whereas, microencapsulated ozone within the microfine bubbles enhances and promoted in-situ stripping of volatile organics and simultaneously terminates normal reversible Henry□s reaction.

Referring now to FIGS. **4**A-**4**B, a microporous diffuser **50** is shown. The microporous diffuser **50** includes a first cylindrical member **56** comprised of a hydrophobic material which provides an outer cylindrical shell for the microporous diffuser **50**. The cylindrical member **56** has a sidewall **56***a* which is comprised of a large plurality of micropores. A second cylindrical member **60** is coaxially disposed within the first cylindrical member **56**. The second cylindrical member **60** is comprised of a hydrophobic material and has a sidewall **60***a* which is comprised of a large plurality of micropores. Also disposed within the confines of the first cylindrical member **56** are a plurality of cylindrical members **58**, here four, which have sidewalls **58***a* having a large plurality of micropores and also comprised of a hydrophobic material.

A proximate end of central cylindrical member **60** is coupled to a first inlet port **52***a* which is provided from a first inlet cap **52** and proximate ends of the plurality of cylindrical members **58** are coupled to second inlet ports generally denoted as **52***b*. At the opposite end of the microporous diffuser **50** an end cap **54** covers distal ends of cylindrical members **56** and **60**. Here distal ends of the plurality of cylindrical members **58** are sealed by separate caps **59** but could be terminated by the end cap **54**. The end cap **54** in conjunction with cap **52** seals the distal ends of the microporous diffuser. Each of the cylindrical members **56**, **58** and **60** are here cylindrical in shape and have a plurality of microscopic openings constructed through sidewalls **56***a*, **58***a* and **60***a*, respectively, thereof having pore sizes matched to or to create a pore size effective for inducing gas/gas reactions in the spring box **30**. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns. The combination of the inlet cap **52** and end cap **54** seals the microporus diffuser **50** permitting liquid and gas to escape by the porous construction of sidewalls of the microporous diffusers.

The microporous diffuser **50** can be filled with a microporous material such as microbeads with mesh sizes from 20 to 200 mesh or sand pack or porous hydrophilic plastic to allow introducing a liquid into the pore spaces where liquid is exiting.

Referring now to FIGS. **5**A and **5**B, an alternate embodiment **70** of a microporous diffuser is shown. The microporous diffuser **70** includes an outer cylindrical member **76** having a sidewall **76***a* within which is disposed an inner cylindrical member **78** having a sidewall **78***a*. The inner cylindrical member **78** is spaced from the sidewall of the outer cylindrical member. The space **77** between the inner and outer cylindrical members **76**, **78** is filled with a packing material comprised of glass beads or silica particles (silicon dioxide) or porous plastic which, in general, are hydrophilic in nature. This space is coupled to an input port **72***b* which receives liquid, and catalysts, and/or nutrients from pump **39** (FIG. **2**). The microporous diffuser **70** has the inner cylindrical member **78** disposed coaxial or concentric to cylindrical member **78**. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns. A proximate end of the inner cylindrical member is coupled to an inlet port **72***a* which is fed an air ozone mixture from pump **36**. The microporous diffuser also includes an end cap **74** which in combination secures distal ends of the cylinders **76** and **78**. The combination of the inlet cap **72** and end cap **74** seals the microporus diffuser permitting liquid and gas to escape by the porous construction of sidewalls of the microporous diffusers.

Referring now to FIGS. **6**A, **6**B, construction details for the elongated cylindrical members for the microporous diffusers **50**, **70** are shown. As shown in FIG. **6**A, sidewalls of the members can be constructed from a metal or a plastic support layer **91** having large (as shown) or fine perforations **91***a* over which is disposed a layer of a sintered i.e., heat fused microscopic particles of plastic. The plastic can be any hydrophobic material such as polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and ABS. The support layer **91** can have fine or coarse openings and can be of other types of materials. FIG. **6**B shows an alternative arrangement **94** in which sidewalls of the members are formed of a sintered i.e., heat fused microscopic particles of plastic. The plastic can be any hydrophobic material such as polyvinylchloride, polypropylene, polyethylene, polytetrafluoroethylene, high density polyethylene (HDPE) and alkylbenzylsulfonate (ABS).

The fittings (i.e., the inlets in FIGS. **4**A, **5**A can be threaded and are attached to the inlet cap members by epoxy, heat fusion, solvent or welding with heat treatment to remove volatile solvents or other approaches. Standard threading can be used for example NPT (national pipe thread) or box thread e.g., (F480). The fittings thus are securely attached to the microporous diffusers in a manner that insures that the microporous diffusers can handle pressures that are encountered with injecting of the air/ozone and liquid.

Referring to FIGS. **7**A-**7**B, an alternate microporous diffuser **90** is shown. The microporous diffuser **90** includes a first cylindrical member **96** comprised of a hydrophobic material which provides an outer cylindrical shell for the microporous diffuser **90**. The cylindrical member **96** has a sidewall **96***a* that is comprised of a large plurality of micro pores. A proximate end of cylindrical member **96** is coupled to a first inlet port **92***a* provided from a first inlet cap **92** and a distal end of the cylindrical member **96** is coupled to an end cap **94** The end cap **94** in conjunction with cap **92** seals the ends of the microporous diffuser **90**. Sidewalls of the cylindrical members **96** is provided with a film of a catalysts or reaction promoter or and absorbing material. Examples include a layer **93** of activated carbon that is abraded into the surface or sintered into the surface. Additionally palladized activated carbon could also be used. As explained above the layer **93** can aid in decomposition of the contaminants in the water. Sidewalls of each of the cylindrical members can have a pore diameter in a range of 1-200 microns, preferably 1-50 microns and more preferably 5-20 microns.

The use of catalysts supported by absorptive materials such as palladized activated carbon can be particularly effective for compounds that have an absorptive affinity to activated carbon. The compounds such as TCE are concentrated near the release location of the ozone micro bubbles, allowing more efficient reaction for water containing lower concentrations of TCE as explained above. The layer **93** can also be provided on the other embodiments **50**, **70** above, e.g., on either or both cylindrical members but preferably on the members that deliver the ozone to the water.

Referring now to FIGS. **8**A and **8**B, an alternate arrangement of a spring box **110** is shown. The spring box **110** includes a circular container **111** comprised of a sidewall **112** of a durable material such as concrete over which is disposed or attached a water tight lid **113** also comprised of concrete. Within the spring box **110** is provided an inlet port **115***a* to receive the water from the spring. Within the circular container are disposed a plurality of microporous diffusers such as those shown in conjunction with my issued U.S. Pat. No. 5,855,775 which is incorporated herein by reference. Alternatively, microporous diffusers **50**, **70**, **90**, as described above in conjunction with FIGS. **4**A and **4**B, FIGS. **5**A and **5**B, or FIGS. **7**A-**7**B may be used.

In the arrangement shown in FIG. **8**A, the microporous diffusers **116** are coupled to a common rotary joint **117** that can provides a gas/ozone feed arrangement **86***a* which can be fed, for example, from compressor/pump **24** and compressor **28** (FIG. **2**).

As shown in FIG. **8**B, the microporous diffusers are arranged in elevation above the bottom of the spring box **110** within a pool **119** of water provided from the spring or other surface water source. The rotary joint **117** enables the microporous diffusers to be rotated in the water enabling the ozone to more effectively mix with the water. The spring box **110** can include a sand or other matrix **120** containing a reaction promoter e.g., catalyst as mentioned.

The spring box **110** is an ozone reactor vessel in which ozone is pumped into the pool of water through the use of the microporous diffusers. The microporous diffusers **116** are disposed in the water under treatment and transfer ozone into the water in the form of micro fine or fine bubbles which promote rapid gas/gas/water reactions with volatile organic compounds particularly in the presence of a catalyst or enhancer which may participate in the gaseous phase of the reaction, instead of solely enhancing dissolved aqueous disassociation and reactions.

In addition, an optional liquid port (not shown) to the rotary joint can be provided to include gas/gas reactions within the gaseous phase as well as inducing water aqueous phased reactions to achieve an overall decomposition rate within the gaseous phase and the aqueous phase from second water reactions. For example, the use of hydrogen peroxide as a laminate coating on the bubbles can enhance decomposition rates as mentioned above.

Referring now to FIG. **9**, an alternative example of the use of the microporous diffusers **50**, **70** is shown. The example shows an injection well to treat subsurface waters of an aquifer. The arrangement includes a well having a casing with an inlet screen and outlet screen to promote a recirculation of water into the casing and through the surrounding ground area. The casing supports the ground about the well. Disposed through the casing is microporous diffusers e.g., **50** or **70**. The injection well treatment system **120** also includes an air compressor **132**, a compressor/pump control mechanism **134**, and an ozone (O_3) generator **136**. The air compressor **134** can feed a stream of air into the microporous diffuser **50** whereas, the compressor pump control **134** feeds a stream of air mixed with ozone (O_3) from the ozone generator **136** into microporous diffuser to affect substantial removal of the above-mentioned or similar types of contaminants. Optionally, or in addition thereto, the treatment system **120** can also include a pump **138** that supplies a liquid decontamination agent such as hydrogen peroxide as well as nutrients and catalyst agents including iron containing compounds such as iron silicates or palladium containing compounds such as palladized carbon. In addition, other materials such as platinum may also be used.

The treatment system **120** makes use of a gas-gas reaction of contaminant vapors and ozone (described below) that can be supplemented with a liquid phase reaction. The use of hydrogen peroxide as a thin film coating on the bubbles promotes the decomposition rate by adding a secondary liquid phase reactive interface as volatile compounds enter the gaseous phase. It also expands the types of compounds that can be effectively removed. Alternatively, the pump control **138** can simply feed water.

In particular, with the microporous diffusers **50** and **70** and use of the optional port to introduce a liquid such as hydrogen peroxide or water into the chamber, the microbubbles are produced in the microporous diffuser by bubbling air/ozone through the central cylinder of the microporous diffusers and into the surrounding outer regions of the microporous diffusers. At the same time, a liquid is introduced into the microporous diffusers **50**, **70** and laminates an outer surface of bubbles formed by the gas. The liquid forms a liquid barrier between the water to be treated and the inside gas containing air/ozone. This arrangement thus can be injected into a slurry containing a catalyst such as silicate, iron silicate, palladium, palladized carbon or titanium dioxide to produce rapid reactions to decompose contaminants within the pool of water contained in the spring box **30**. The reactions can proceed as set out below.

The process uses microfine bubble injection to produce simultaneous extraction/decomposition reactions as opposed to simply creating smaller and smaller sized bubbles for the purpose of injecting into free water. The process involves generation of fine bubbles which can promote rapid gas/gas/water reactions with volatile organic compounds which a substrate (catalyst or enhancer) participates in, instead of solely enhancing dissolved (aqueous) disassociation and reactions. The production of microbubbles and selection of appropriate size distribution is provided by using microporous material and a bubble chamber for optimizing gaseous exchange through high surface area to volume ratio and long residence time within the liquid to be treated. The equipment promotes the continuous production of microbubbles while minimizing coalescing or adhesion.

The injected air/liquid combination moves as a fluid into the water to be treated. The use of microencapsulated ozone enhances and promotes in-situ stripping of volatile organics and simultaneously terminates the normal reversible Henry's reaction. The process involves promoting simultaneous volatile organic compounds (VOC) in-situ stripping and gaseous decomposition, with moisture (water) and substrate (catalyst or enhancer). The reaction mechanism is not a dissolved aqueous reaction. In some cases, with cis- or trans-DCE, the aqueous phase reaction may assist the predominantly gas-phase reaction.

The remote process controller and monitor allows for the capability for sensor feedback and remote communication to the pump control **24** and ozone (or oxygen or both) generator **26** to achieve a certain level of gaseous content (e.g., dissolved oxygen, ozone, or other gas) and rate of mixing to promote efficient reactions. This is done by sensors **39** (FIGS. **3**A, **3**B) placed in the bubble chambers at certain distances from the microporous diffusers **50**, **70**. Oxygen content, redox potential, and dissolved VOC concentration of the water can be monitored within the treatment system. The operator can access the information, modify operations and diagnose the condition of the unit by telephone modem or satellite cell phone. This provides on-site process evaluation and adjustment without the need of on-site operator presence.

Appropriately sized microfine bubbles can be generated in a continuous or pulsing manner which allows alternating water/bubble/water/bubble fluid flow. The microfine bubbles substantially accelerate the transfer rate of volatile organic compounds like PCE from aqueous to gaseous state. Reducing the size of the bubbles to microfine sizes, e.g., 5 to 50 microns, can boost extraction rates. These sizes boost exchange rates and do not tend to retard rise time by too small a size. When an oxidizing gas (ozone) is added into the microbubbles, the rate of extraction is enhanced further by maintaining a low interior (intrabubble) concentration of PCE, while simultaneously degrading the PCE by a gas/gas/water reaction. The combination of both processes acting simultaneously provides a unique rapid removal system which is identified by a logarithmic rate of removal of PCE, and a characteristic ratio of efficiency quite different from dissolved (aqueous) ozone reactions. The compounds commonly treated are HVOCs (halogenated volatile organic compounds), PCE, TCE, DCE, vinyl chloride (VC), petroleum compounds (BTEX: benzene, toluene, ethylbenzene, xylenes).

An analysis of the reaction mechanism is set out. Gaseous exchange is proportional to available surface area. With partial pressures and mixtures of volatile gases being held constant, a halving of the radius of bubbles would quadruple (i.e., times) the exchange rate. If, in the best case, a standard well screen creates air bubbles 200 times the size of a medium sand porosity, a microporous diffuser of 5 to 20 micron size creates a bubble 1/10 the diameter and six to ten times the volume/surface ratio as shown in Table 1.

TABLE 1

Diameter (microns)	Surface Area 4π	Volume $4/3\ \pi$	Surface Area/ Volume
200	124600	4186666	0.03
20	1256	4186	0.3

Theoretically, the microporous bubbles exhibit an exchange rate of ten times the rate of a comparable bubble from a standard ten slot well screen.

TABLE 2

	Surface to Volume (A/V) Ratio Changes As Function of Bubble Size As Bubble Volume Increases							
D (i.e.,2r) or h as Fraction of Pore Size	0.1	0.25	0.5	1	2	5	10	20
Sphere						SPHERIOD		
Area = 4 πr^2	0.0314	0.19625	0.785	3.14	18.8	37.7	69	131
Vol = 4/3 πr^3	0.0005	0.00817	0.065	0.53	6.3	15.7	31	62
Ratio	62	24	12	5.9	3	2.4	2.2	2.1

In wastewater treatment, the rate of transfer between gas and liquid phases is generally proportional to the surface area of contact and the difference between the existing concentration and the equilibrium concentration of the gas in solution. Simply stated, if the surface to volume ratio of contact is increased, the rate of exchange also increases as illustrated in Table 2. If, the gas (VOC) entering the bubble (or micropore space bounded by a liquid film), is consumed, the difference is maintained at a higher entry rate than if the VOC is allowed to reach saturation equilibrium. In the case of a halogenated volatile organic carbon compound (HVOC), PCE, gas/gas reaction of PCE to by-products of HCl, CO_2 and H_2O accomplishes this. In the case of petroleum products like BTEX (benzene, toluene, ethylbenzene, and xylenes), the benzene entering the bubbles reacts to decompose to CO_2 and H_2O. The normal equation for the two-film theory of gas transfer is:

$$r_m = K_g A(C_g - C)$$

where:

r_m=rate of mass transfer

K_g=coefficient of diffusion for gas

A=area through which gas is diffusing

C_g=saturation concentration of gas in solution

C=concentration of gas in solution.

The restatement of the equation to consider the inward transfer of phase change from dissolved HVOC to gaseous HVOC in the inside of the bubble would be:

C_S=Saturation concentration of gas phase of HVOC or VOC in bubble.

C=Initial concentration of gaseous phase of HVOC or VOC in bubble volume.

Soil vapor concentrations are related to two governing systems: water phase and (non-aqueous) product phase. Henry□s and Raoult□s Laws are commonly used to understand equilibrium-vapor concentrations-governing volatilisation from liquids. When soils are moist, the relative volatility is dependent upon Henry□s Law. Under normal conditions (free from product) where volatile organic carbons (VOCs) are relatively low, an equilibrium of soil, water, and air is assumed to exist. The compound tetrachloroethene (PCE) has a high exchange capacity from dissolved form to gaseous form. If the surface/volume ratio is modified at least ten fold, the rate of removal should be accelerated substantially.

FIG. **10** shows a plot of removal rate of PCE for an aqueous solution equivalent to 120 ppb, over differing bubble sizes. The air volume and water volume is held constant. The only change is the diameter of bubbles passed through the liquid from air released from a diffuser.

Ozone is an effective oxidant used for the breakdown of organic compounds in water treatment. The major problem in effectiveness is that ozone has a short lifetime. If ozone is mixed with sewage containing water above ground, the half-life is normally minutes. Ozone reacts quantitatively with PCE to yield breakdown products of hydrochloric acid, carbon dioxide, and water.

To offset the short life span, the ozone is injected with microporous diffusers, enhancing the selectiveness of action of the ozone. By encapsulating the ozone in fine bubbles, the bubbles would preferentially extract volatile compounds like PCE from the mixtures of soluble organic compounds they encountered. With this process, volatile organics are selectively pulled into the fine air bubbles. Gas entering a small bubble of volume ($4\pi r^3$) increases until reaching an asymptotic value of saturation. If we consider the surface of the bubble to be a membrane, a first order equation can be written for the monomolecular reaction of the first order. The reaction can be

$$\frac{dx}{dt} = K(Q - X)$$

written as follows:

where X is the time varying concentration of the substance in the bubble, Q is the external concentration of the substance, and K is the absorption constant.

$$X = Q(l - e^{Kt})$$

If at time t=0, X=0, then:

$$K = \frac{dx/dt}{Q - X}$$

The constant K is found to be:

By multiplying both numerator and denominator by V, the

$$K = \frac{vdx/dt}{v(Q - X)}$$

volume of the bubble, we obtain

which is the ratio between the amount of substance entering the given volume per unit time and quantity V(Q−X) needed to reach the asymptotic value. By analyzing the concentration change within the fine bubbles sent through a porous matrix with saturated (water filled) solution interacting with the matrix (sand), and determining the rate of decomposition of the products (TCE+ozone=CO_2+HCl) and (Benzene+ozone=CO_2+HOH), the kinetic rates of reaction can be characterized.

The rate which the quantity k_1QV of the substance flows in one unit of time from aqueous solution into the bubble is proportional to Henry□s Constant. This second rate of decomposition within the bubble can be considered as k_1, a second

$$\frac{dx}{dt} = k_1Q - k_2X$$

rate of reaction ($-k_2X$), where

$$X = \frac{k_1}{k_2}Q$$

and, at equilibrium, as $dx/dt=0$, gives

However, if the reaction to decompose is very rapid, so $-k_2X$ goes to zero, the rate of reaction would maximize k_1Q, i.e., be proportional to Henry□s Constant and maximize the rate of extraction since VOC saturation is not occurring within the bubbles.

The combination of microbubble extraction and ozone degradation can be generalized to predict the volatile organic compounds amenable to rapid removal. The efficiency of extraction is directly proportional to Henry□s Constant. Multiplying the Henry□s Constant (the partitioning of VOCs from water to gas phase) times the reactivity rate constant of ozone for a particular VOC yields the rate of decomposition expected by the microbubble process.

The concentration of HVOC expected in the bubble is a consequence of rate of invasion and rate of removal. In practice, the ozone concentration is adjusted to yield 0

$$r_{voc} = -K_La_{voc}(C - C_L)$$

concentration at the time of arrival at the surface.

where:

f_{voc}=rate of VOC mass transfer, (μg/ft^3□h)

$(K_1a)_{voc}$=overall VOC mass transfer coefficient, (1/h)

C=concentration of VOC in liquid

C_L=saturation concentration of VOC in liquid μg/ft^3 (μg/m^3)

The saturation concentration of a VOC in wastewater is a function of the partial pressure of the VOC in the atmosphere in contact with the wastewater.

$$\frac{c_g}{C_L} = H_c \text{ thus, } C_g = H_C \cdot C_L$$

C_g=concentration of VOC in gas phase μg/ft^3 (μg/m^3)

C_L=saturation concentration of VOC in liquid μg/ft^3 (μg/m^3)

H_c=Henry□s Constant

The rate of decomposition of an organic compound C_g (when present at a concentration (C) by ozone can be formulated

$$-\left(\frac{dC_g}{dt}\right)O_3 = K_{oc}(O_3)(C_g)$$

by the equation:

or, after integration for the case of a batch reactor:

$$-\ln\left(\frac{C_{g\,end}}{C_{g_o}}\right) = K_{o_c}(O_3)t \qquad \text{(equation 2)}$$

$$(C_g)_{end} = C_oe_{oc}^{-K}(O_3)t$$

$$\frac{(C_g)_{end}}{(C_g)_o} = e_{o_c}(O_3)t$$

where

(O_3)=concentration of ozone averaged over the reaction time (t)

$(C_g)_o$=halocarbon initial concentration

$(C_g)_{end}$ =halocarbon final concentration

Substituting:

rm=K_gA (C_g–C) From Henry□s Law:

rm=K_gA ((H_g·C_g) C)–C_g=H_c·C_g (equation 3)

rm=K_gZ ((H_g·C_g)–C) With ozone

$$rm = K_gZ((H_c \cdot C_g) - C - K_o(O_3)(C_g))(Hg \cdot C) - K_o(O_3)(C_g) = 0 \qquad \text{(equation 4)}$$

Rate of decomposition is now adjusted to equal the total HVOC entering the bubble.

$$\text{SET: } (H_c \cdot C_g) = Ko(O_3)\ (C_g) \qquad \text{(equation 5)}$$

therefore surface concentration=0

This condition speeds up the rate of extraction because the VOC never reaches equilibrium or saturation in the bubble.

Table 4 gives the Henry□s Constants (H_c) for a selected number of organic compounds and the second rate constants (R_2) for the ozone radical rate of reaction in solely aqueous reactions where superoxide and hydroxide reactions dominate. The third column presents rates of removal process.

TABLE 4

REMOVAL RATE COEFFICIENTS

Organic Compound	Ozone Aqueous Second Order Rate Constant (a.) (M^{-1} SEC^{-1})	Henry□s Constant (b.)	Rate Removal Coefficient (τ) (c.)
Benzene	2	5.59×10^3	0.06
Toluene	14	6.37×10^3	0.07
Chlorobenzene	0.75	3.72×10^3	0.013
Dichloroethylene	110	7.60×10^3	0.035
Trichloroethylene	17	9.10×10^3	0.05
Tetrachloroethylene	0.1	25.9×10^3	0.06
Ethanol	0.02	$.04 \times 10^3$	0.0008

(a.) From Hoigne and Bader, 1983. □Rate of Constants of Direct Reactions of Ozone with Organic and Inorganic Compounds in Water-I. Non-dissociating Compounds□ Water Res/ 17: 173-184.

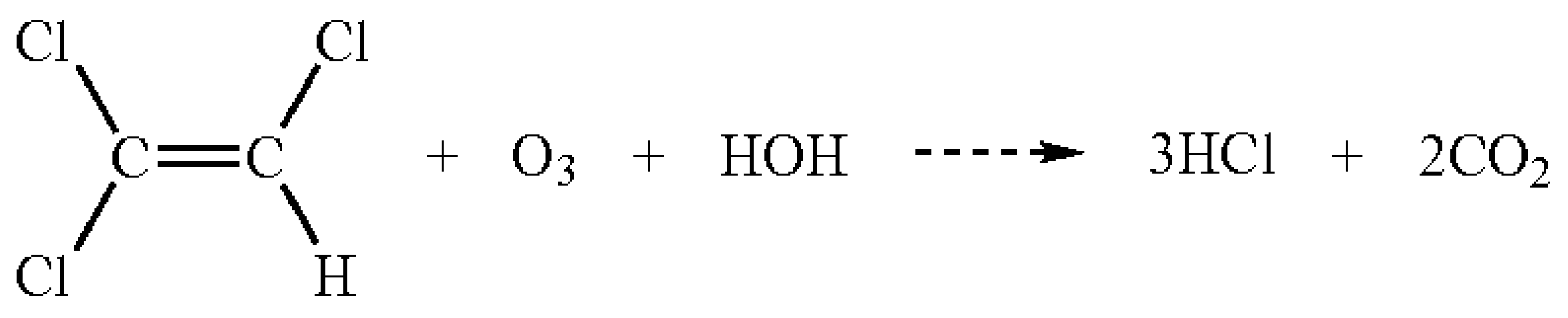
(b.) From EPA 540/1-86/060, Superfund Public Health Evaluation Manual EPA 540/1-86/060 (OSWER Directive 9285.4-1) Office of Emergency and Remedial Response, Office of Solid Waste and Emergency Response.

(c.) See U.S. Pat. No. 5,855,775.

The rapid removal rate of this process does not follow Hoigne and Bader (1983) rate constants. However, there is a close correlation to Henry□s Constant as would be expected from equation 5. The presence of the substrate (sand) and moisture is necessary to complete the reaction. The active ingredient in the sand matrix appears to be an iron silicate. The breakdown products include CO_2 and dilute HCl.

Two sets of equations are involved in the reactions:

Dissolved Halogenated Compounds



Dissolved Petroleum Distillates

$$C_6H_{12} + 6O_3 \xrightarrow[\text{Substrate}]{HOH} 6CO_2 + 6HOH$$

Exemplary compounds are normally unsaturated (double bond), halogenated compounds like PCE, TCE, DCE, Vinyl Chloride, EDB; or aromatic ring compounds like benzene derivatives (benzene, toluene, ethylbenzene, xylenes). Also, pseudo Criegee reactions with the substrate and ozone appear effective in reducing certain saturated olefins like trichloro alkanes (1,1,-TCA), carbon tetrachloride (CCl_4), chloroform and chlorobenzene, for instance.

The following characteristics of the contaminants appear desirable for reaction:

Henry□s Constant:	10^{-2} to 10^{-4} $m^3 \cdot atm/mol$
Solubility:	10 to 20,000 mg/l
Vapor pressure:	1 to 3000 mmhg
Saturation concentration:	5 to 9000 g/m^3

Absorption-Destruction

Absorptive substrates like activated carbon and certain resins serve to remove disolved volatile organic carbon compounds by absorption to the surface. The active surface of particles contain sites which the compounds attach to. The surface absorption is usually mathematically modeled by use of a Langmuir or Freunlich set of equations for particular sizes of particles or total surface area if the material is presented in cylinders or successive plates.

The derivation of the Langmuir isotherm stipulated a limited number of absorption sites on the surface of the solid. The absorption of a solute on the surface necessitates the removal of a solvent molecule. An equilibrium is then reached between the absorbed fraction and the remaining concentration in solution. If a continual gas phase of microbubbles is being released from a porous surface, can remove the absorbed molecule and decompose it, the reaction would be moved along much faster than in aqueous phase without the collecting surface.

$$Q_l = \frac{K_{L1} C_{L1}}{1 + K_{L1} C_{L1}}$$

Q_1=fractional surface coverage of solute
K_{L1}=equilibrium constant
C_{L1}=solute concentration

What is claimed is:

1. A method comprises:

forming microbubbles including an oxidizing gas entrapped by water and having a coating of hydrogen peroxide over the microbubbles to provide microbubbles including the oxidizing gas having the hydrogen peroxide coating to treat contaminants.

2. The method of claim **1** wherein the microporous bubbles are introduced using a microporous diffuser.

3. The method of claim **2** wherein the microporous diffuser includes a nutrient agent and/or a catalyst agent to contact and become carried by the microbubbles.

4. The method of claim **1** wherein the microbubbles have a diameter of less than 200 microns.

5. The method of claim **1** wherein oxidizing gas is ozone.

6. The method of claim **1** wherein oxidizing gas is oxygen.

7. The method of claim **1** wherein the oxidizing gas includes ozone and air in the microbubbles with the ozone.

8. The method claim **1** wherein forming the microbubbles comprises:

introducing an air-ozone stream through a first plurality of centrally disposed members, having sidewalls of microporous material; and

introducing a liquid including hydrogen peroxide through a space between the first plurality of centrally disposed members and a second member that surrounds the first plurality of centrally disposed members, and which is in fluid communication with the first plurality of centrally disposed members, to coat surfaces of microbubbles entrapping air-ozone exiting the first plurality of centrally disposed members with a coating of the hydrogen peroxide.

9. The method claim **1** wherein forming the microbubbles comprises:

introducing an air-ozone stream through a first centrally disposed member, having sidewalls of a microporous material; and

introducing a liquid including hydrogen peroxide through a space between the first centrally disposed member and a second member that surrounds the first centrally disposed member, and which is in fluid communication with the first centrally disposed member, the first and second members disposed in a wet soil formation, and the first member to produce microbubbles entrapping air-ozone and the second member to coat surfaces of the microbubbles with a coating of the hydrogen peroxide.

10. The method of claim **1** wherein the microbubbles have a diameter within a range of about 1-50 microns.

11. The method of claim **1** wherein the microbubbles have a diameter in a range of about 5-20 microns.

12. The method of claim **9** wherein the space between the first and second members is filled with a hydrophilic packing material.

13. The method of claim **9** wherein space between the first and second members is filled with a packing material comprised of glass beads, silica particles or porous plastic, and receives the hydrogen peroxide.

14. A method comprises:

forming microbubbles of an oxidizing gas with the microbubbles having a coating of hydrogen peroxide by introducing the oxidizing gas through a microporous diffuser disposed in contact with water; and

contacting the microbubbles with the hydrogen peroxide.

15. The method of claim **14** wherein the microporous diffuser includes a nutrient agent and/or a catalyst agent to contact and become carried by the microbubbles.

16. The method of claim **14** wherein the microbubbles have a diameter of less than 200 microns.

17. The method of claim **14** wherein the oxidizing gas is ozone.

18. The method of claim **14** wherein oxidizing gas is oxygen.

19. The method of claim **14** wherein the oxidizing gas includes ozone, and included in the microbubbles with the ozone is air.

20. The method claim **14** wherein forming the microbubbles comprises:

introducing an air-ozone stream through the microporous diffuser, the microporous diffuser having a first, centrally disposed member with sidewalls comprised of a microporous material, and a second member that surrounds the first, centrally disposed member and which is in fluid communication with the first, centrally disposed member; and

introducing a liquid including hydrogen peroxide through a space between the first centrally disposed member and the second member, with the first and second members disposed in a wet soil formation, with the first member to produce microbubbles entrapping air-ozone, and the second member to coat surfaces of the microbubbles with the coating of the hydrogen peroxide.

21. The method claim **14** wherein forming the microbubbles comprises:

introducing an air-ozone stream through a first plurality of centrally disposed members, having sidewalls of microporous material; and

introducing a liquid including hydrogen peroxide through a space between the first plurality of centrally disposed members and a second member that surrounds the first plurality of centrally disposed members, and which is in fluid communication with the first plurality of centrally disposed members, to coat surfaces of microbubbles entrapping air-ozone exiting the first plurality of centrally disposed members with a coating of the hydrogen peroxide.

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